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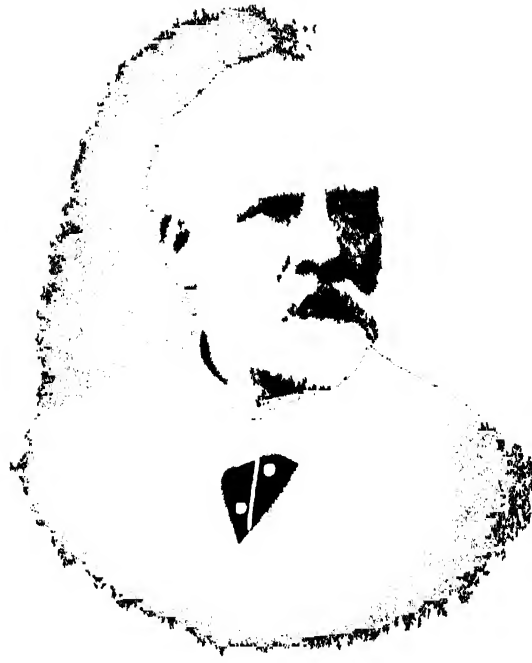

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ANHYDROUS ALUMINUM CHLORIDE

in

ORGANIC CHEMISTRY

By

CHARLES ALLEN THOMAS

[illegible] THE THOMAS AND HOCHWALT LABORATORIES, MONSANTO CHEMICAL COMPANY

In collaboration with

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AND ROSS W. MOSHIER

THOMAS AND HOCHWALT LABORATORIES,
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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie, Moissan's Traité de Chimie Minérale Générale, Friend's and Mellor's Textbooks of Inorganic Chemistry and Heilbron's Dictionary of Organic Compounds, it often takes a great deal of time to coördinate the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing

to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

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Preface

More than six decades have passed since Friedel and Crafts published their first papers on the synthesis that bears their name. Little did they realize that from their "accidental observance of the action of metallic aluminum on amyl chloride" would evolve the Friedel-Crafts reaction as we know it today– a tool applicable to the preparation of many types of compounds and destined to play a large role in organic chemistry. At present, reactions involving the use of anhydrous aluminum chloride are so numerous and so diverse that it has been recognized as an important factor in organic chemistry.

During past years the number of investigators in this field and the amount of material on this subject have grown enormously. It is a difficult task for an average individual worker to collect this widely scattered literature and to have in one place all the available material. Here is the purpose of this volume. Every effort has been made to make it complete and to include all references of published material, both of a purely scientific and industrial nature, including the available patent literature.

I am deeply indebted to my collaborators, Mary B. Moshier, Ross W. Moshier and Herbert E. Morris, for their valuable and untiring assistance in the preparation of this volume. The kind help of many other people is also gratefully acknowledged, including Harrison E. Howe who fostered the beginning of the book, Costin D. Nenitzescu for his personal communications, Austin M. Patterson for reviewing nomenclature, Philip H. Groggins for reviewing the manuscript and offering valuable suggestions, Robert E. Burk for submitting valuable material on halide catalysis, and Herman A. Bruson for contributions on the synthesis of keto-acids.

A great many people, as seen in the text, have sent in reprints and personal communications; this list is too great to enumerate, but I wish to extend them my thanks. Also it is a pleasure to acknowledge the many contributions to the text made by members of this laboratory. I particularly wish to thank Doris Binkley and Kathleen Flahive for proofreading and Barbara Southard for typing. Finally, the cooperation of G. G. Hawley, Reinhold Publishing Corporation, is greatly appreciated.

CHARLES ALLEN THOMAS

Dayton, Ohio
July 11, 1941

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Chapter 1

Introduction

The role of anhydrous aluminum chloride in organic chemistry is generally associated with syntheses in which hydrogen halide is evolved. The reaction, involving loss of a hydrogen atom from an aromatic nucleus and a halogen atom from another compound to yield a condensation product, was announced by Friedel and Crafts as "a new method for the preparation of aromatic hydrocarbons." In the last decade, the Friedel-Crafts reaction has been extended to similar replacement of cycloaliphatic or aliphatic hydrogen.

Orientation and degree of reactivity in Friedel-Crafts reactions are similar to that observed in other reactions involving substitution in aromatic nuclei. The presence of positive groups, for example, alkyl- and alkoxy-, facilitates substitution; whereas electronegative groups like carbonyl-, carboxy-, and nitro- have an inhibiting effect. Polynuclear hydrocarbons and the so-called "super-aromatic" heterocyclic compounds, thiophene and furan, undergo the reaction. Friedel-Crafts reactions do not proceed readily with most heterocyclic compounds of nitrogen. As the aromaticity of a compound increases, either through the presence of activating groups or through the type of ring-structure, electronegative substituents exert less of an inhibiting effect.

These restrictions do not apply to the organic halogen component; thus, there is but little difference in the reactivity of positively or negatively substituted acid halides. Most aliphatic and arylalkyl halogen compounds and many halogenated compounds of sulfur, selenium, arsenic, and phosphorus undergo the reaction. Nuclear halogen is replaced only in exceptional instances.

Intramolecular ring closure, with evolution of hydrogen chloride, is effected by the action of aluminum chloride on certain arylalkyl halides and acid halides.

Friedel and Crafts also found that aluminum chloride catalyzes the addition of acid anhydrides to aromatic hydrocarbons. This reaction, like the Friedel-Crafts condensations in which hydrogen halide is evolved, has been extended to various substituted aromatic hydrocarbons and to reactive heterocyclic compounds. It has been applied largely to the preparation of keto-acids by addition of dicarboxylic acid anhydrides to an aromatic compound. The reaction of anhydrides of monobasic acids and aromatic compounds has been more recently found to afford an excellent method for the preparation of arylalkyl ketones.

Shortly after the announcement of aluminum chloride-catalyzed reactions with organic halides, it was found that olefinic hydrocarbons could

replace alkyl halides as alkylating agents for the preparation of benzene homologs. The reaction has been extended to the addition of olefinic acids, esters, and ketones to aromatic hydrocarbons, and to intramolecular ring closures of arylalkyl compounds having an olefinic double bond. Addition of aromatic compounds to alkylene oxides and the alkylation of aromatic hydrocarbons with paraffins and cycloparaffins are comparatively new developments.

The reaction of sulfur with aromatic hydrocarbons in the presence of aluminum chloride furnishes an effective method for the preparation of polynuclear sulfur compounds. The production of sulfones from sulfur dioxide and aromatic compounds has been extensively investigated. In the presence of hydrogen chloride, carbon monoxide or hydrogen cyanide reacts with aromatic compounds to yield aldehydes. Addition of aromatic compounds also has been shown to take place at the unsaturated cyanide radical.

In their study of the disruptive action of aluminum chloride on hydrocarbons, Friedel and Crafts noted its dehydrogenating effect. Today, the dehydrogenating condensation of aromatic hydrocarbons is a widely used method for the synthesis of polynuclear compounds.

Dehydrating condensations are also effected with aluminum chloride. Alkylation of aromatic compounds may be effected with primary, secondary, or tertiary alcohols. Other alkylating or acylating reagents which have been used include carboxylic acids, esters and ethers. A wide miscellany of dehydrating condensations comprises reactions which involve replacement of oxygen from carbonyl- and carboxy- groups.

The disruptive effect of aluminum chloride has been utilized not only in petroleum cracking but also in syntheses involving rearrangement, migration, and cleavage, such as the Fries transformation of aromatic esters to hydroxy-ketones, alkylation by transfer of an alkyl group from one aromatic nucleus to another, and preparation of phenols from the corresponding phenol ethers.

The polymerizing activity of aluminum chloride is of commercial importance in the preparation of lubricants and motor fuels from lower boiling hydrocarbons and in the production of synthetic resins from unsaturated hydrocarbons. In its role as polymerizing catalyst it has served as a refining agent in removing polymerizable constituents from petroleum hydrocarbons.

It is obvious that the reaction announced by Friedel and Crafts as "a new method for the preparation of aromatic hydrocarbons" has been extensively applied to many other fields of organic chemistry. Many of the mechanisms involved have been studied, and intensive investigations have been directed at the determination of optimum conditions. Today we have in aluminum chloride an extremely effective catalyst for syntheses in aromatic and aliphatic chemistry.

A number of excellent reviews dealing with the scientific and commercial importance of aluminum chloride in organic synthesis are available.[1]

[1] N. O. Calloway, *Chem. Rev.*, 17, 327-392 (1935). P. H. Groggins, "Unit processes in organic synthesis," p. 634-691, 1938; *Ind. Eng. Chem.*, 23, 152-160 (1931); *Trans. Am. Inst. Chem. Engrs.* New Orleans meeting, 1930, 44 p. (Advance copy); *C. A.*, 25, 687. G. Kranzlein, *Metallborse*, 1856-1857 (1930); *C. A.*, 25, 28. P. Kranzlein, *Angew. chemie*, 51, 373-379 (1938). G. Kranzlein, "Aluminum chlorid in der organischen chemie," 281 pp., 1939; C. D. Nenitzescu, *Angew. chemie*, 231-238 (1939). P. J. Montagne, *Chem. Weekblad*, 11, 305-322 (1914); *C. Z.*, 1924, I, 1645.

Chapter 2

Historical Sketch of Charles Friedel and James Mason Crafts[1]

Although Charles Friedel and James Mason Crafts are best remembered by the reaction which bears their names, their work on the use of aluminum chloride in organic synthesis played a comparatively minor role in their lives.

Charles Friedel, born in Strasbourg, Alsace, on March 12, 1832, was forty-five years old at the time of the first announcement of the Friedel-Crafts reaction. At the time he was professor of mineralogy in the School of Mines at the Sorbonne. The work with aluminum chloride had been done in a small laboratory which was attached to the professorship. His previous researches had covered a wide range, including such very diverse fields as aldehydes and ketones, secondary alcohols, pinacone, lactic acid, theory of double decomposition, organic and inorganic compounds of silicon, mixed halogen compounds of hydrocarbons, and the synthesis of glycerol from propylene through chlorohydrin. This wide divergence of interests is exemplified in the fact that in 1869 he had presented two dissertations for his doctorate degree, one on aldehydes and ketones and the other on the pyroelectric properties of crystals. His interest in mineralogy may be traced to early encouragement which was given to him by his maternal grandfather, George Louis Duvernoy, professor at the Museum of Natural History at Paris. The unwavering devotion to organic chemistry which was his had been instilled in him by Wurtz, whose laboratory he had entered in 1854. In the small laboratory, housed in the School of Medicine, and providing accommodations for only sixteen students, a long friendship was initiated which remained a directing force in Friedel's life.

James Mason Crafts, born of American parents in Boston, Massachusetts, on March 8, 1839, was twenty years old when he went to Freiburg, Saxony, to pursue further an early developed interest in mineralogy and mining engineering. A year later he went to Heidelberg where he worked under Bunsen, who had just begun his research on spectroscopy. Here his interest in chemistry, aroused at Freiburg, was decidedly increased. Accordingly, in 1861, he went to Paris and worked under Wurtz in the small laboratory in the School of Medicine. He met Charles Friedel at this time, and their joint interest in mineralogy and organic chemistry bore fruit in a series of researches on the organic compounds of silicon.

[1] J. M. Crafts, "Friedel Memorial Lecture," *J. Chem. Soc.*, 77, 993-1019 (1900); James Mason Crafts, obituary, *J. Am. Chem. Soc. (Proceedings)*, 39, 171-178 (1917). A. A. Ashdown, "Earliest History of the Friedel-Crafts Reaction," *Ind. Eng. Chem.*, 19, 1063-1065 (1927).

Realizing, however, that his years abroad were meant only as a preliminary to his life's work, he returned to the United States in 1865, and after a year's travel spent in the examination of mines in Mexico and the West, he became the first professor in chemistry at Cornell University. In 1870 he succeeded Professor Storer in the chair of general chemistry at the Massachusetts Institute of Technology, but four years later ill health obliged him to give up active teaching, and he returned to Paris. Here most of his time was spent in research at the School of Mines and in the laboratory of Wurtz.

It was only natural that Friedel and Crafts, uniquely bound as they were to both mineralogy and organic chemistry, should revive their former collaborative scheme of research.

The discovery of the use of aluminum chloride as a catalyst for organic reactions sprang from an "accidental observation of the action of metallic aluminum on amyl chloride." Friedel and Crafts soon realized that it was the metallic halide rather than the metal which was the activating body, and within five or six weeks had verified the catalytic effect of aluminum chloride as an agent for alkylation or acylation of aromatic hydrocarbons by reaction with alkyl or acyl chlorides. The results obtained in the very beginning seemed to show that any number of halogen atoms in a paraffin could be replaced by a phenyl group, that the six hydrogen atoms in the benzene ring could each be replaced successively by alkyl, and that a halogen in an aromatic side chain acted with even more readiness on the benzene ring. Ketones could be prepared by reacting chlorides of aliphatic or aromatic mono- or di-basic acids with benzene and its homologs. A method for the preparation of a host of new compounds was thus revealed in the first papers.

A summary of papers presented by Friedel and Crafts on reactions with aluminum chloride is given at the end of this chapter. It will be seen that the greater part of the work was done in 1877 and 1878, although occasional articles, dealing chiefly with more detailed work on previously announced reactions, appeared until 1898. There were a number of reasons for the little work done by Friedel and Crafts on the aluminum chloride reaction after 1879. In that year Friedel, as professor of mineralogy, began a series of some thirty papers on the synthesis of artificial minerals. These researches, coupled with the fact that Friedel and Crafts had at the time only a very small laboratory with no place for students or assistants, retarded progress in fitting the Friedel-Crafts reaction to new fields.

Upon the death of Wurtz, in 1884, Friedel succeeded him as professor of organic chemistry at the Sorbonne. Although Friedel's revived interest in the aluminum chloride reaction is attested by the comprehensive summary which appeared in that year, a severe illness in 1885 retarded his capacity for experimental work during his remaining years. The second part of the summary did not appear until 1888. Three years later the close association of Friedel and Crafts was broken upon the latter's return to the United States. Before his death, Wurtz had succeeded in obtaining

permission for the construction of new laboratories. Friedel's attention was perforce turned to the planning and equipping of these units, which were officially opened in 1895.

Friedel died on April 20, 1899. From the Friedel Memorial Lecture, presented to the Chemical Society by Crafts, the following shows Crafts' esteem for his associate: "During the thirty-eight years in which a close friendship made him a witness of conduct and actions, the writer cannot recall a single instance in which he would have wished his friend to have thought or acted otherwise than he did."

At the time of Friedel's death, Crafts was president of the Massachusetts Institute of Technology, which since his return to America in 1891 he had served in turn as professor of organic chemistry, head of the department of chemistry, and member of the Corporation of the Institute. Finding that the duties of the presidency left him too little time for science, he resigned this office in 1900, retaining a research laboratory at the Institute. Although his declining health greatly interfered with his activity he made notable contributions to thermometry and the study of catalysis in solutions during this time. He died on June 20, 1917.

Although the greater part of Friedel and Crafts' work on reactions catalyzed by aluminum chloride was done in the course of a few years, it forms a substantial foundation to the reactions which are discussed in this book. They noted the following distinct fields of applications:

Reaction of organic halides with aromatic hydrocarbons
Reaction of anhydrides of organic acids with aromatic hydrocarbons
Reaction of oxygen, sulfur, sulfur dioxide, carbon dioxide, and phosgene with aromatic hydrocarbons
Cracking of aliphatic and aromatic hydrocarbons
Polymerization of unsaturated hydrocarbons

The Friedel-Crafts reaction today has become a widely accepted method for alkylation and acylation of aromatic hydrocarbons. Friedel and Crafts' patent "Improvements in the Treatment of Hydrocarbons for Their Purification and Conversion into Other Products"[2] was probably the first of the numerous patents which deal with the use of aluminum chloride in the petroleum industry. The polymerizing activity of aluminum chloride has been likewise broadly utilized.

A chronological list of papers presented by Friedel and Crafts on reactions catalyzed by aluminum chloride is given in the following summary:

On May 18, 1877, it was reported[3] at the meeting of the Société Chimique de Paris that Friedel and Crafts had commenced the study of the action of aluminum chloride on various chlorides, hydrocarbons, and mixtures of various compositions. It was announced that they had found that aluminum chloride reacts in the cold with amyl chloride with pro-

[2] British P 4 769 (1877) to C. D. Abel (a communication from abroad by Charles Friedel and James M. Crafts).
[3] C. Friedel and J. M. Crafts, *Bull. soc. chim (2)*, **27**, 530 (1877).

duction of hydrogen chloride, hydrocarbons of the composition C_nH_{2n+2} and highly condensed hydrocarbons. When petroleum was treated with aluminum chloride, gas was evolved, and condensation products were formed. With a mixture of an organic chloride and an aromatic hydrocarbon, reaction occurred with formation of such alkylation products as toluene, ethylbenzene, or amylbenzene and acylation products like benzophenone.

Previously, Zincke [4] had announced the reaction of aromatic hydrocarbons with halogen compounds in the presence of zinc dust:

$$2C_6H_5H + 2ClCH_2.C_6H_5 \xrightarrow{Zn} 2C_6H_5.CH_2.C_6H_5 + 2HCl$$

The fact that aluminum chloride catalyzed the same reaction pointed to catalysis by intermediately formed zinc chloride in the Zincke reaction.

Friedel and Crafts summarized the reactions effected in presence of aluminum chloride as follows:

$$CH_3Cl + C_6H_6 = HCl + C_6H_5CH_3$$
$$C_6H_5CH_2Cl + C_6H_6 = HCl + C_6H_5CH_2C_6H_5$$
$$C_6H_5COCl + C_6H_6 = HCl + C_6H_5COC_6H_5$$
$$2CH_3Cl + C_6H_6 = 2HCl + C_6H_4(CH_3)_2$$

In a paper [5] presented on June 11, 1877, to L'Acadamie des Sciences, Friedel and Crafts again described their new general method for the synthesis of aromatic hydrocarbons, noting that organic halides in general may be used as alkylating agents.

Friedel and Crafts' third general note [6] was presented to L'Academie des Sciences in the same year by Wurtz. The use of other metallic chlorides was mentioned, and it was pointed out that the action of chloride depends upon the amount of hydrogen chloride which can be liberated. Ferric chloride had been found to cause the evolution of almost as much hydrogen chloride as does aluminum chloride, but ferrous chloride had been found to be inferior. The replacement of organic halides by inorganic halides was indicated; thus phosphorus trichloride heated with benzene and aluminum chloride gave an organic compound of phosphorus. The following mechanism for the reaction of amyl chloride with benzene was suggested:

$$C_5H_{11}Cl + C_6H_6Al_2Cl_5 = Al_2Cl_6 + C_6H_5C_5H_{11}$$

At the June 15, 1877, meeting of the Société Chimique de France, Friedel and Crafts [7] described the reaction of chloroform or carbon tetrachloride on benzene in the presence of aluminum chloride. They noted that aluminum bromide and aluminum iodide also catalyzes the reaction. In an accompanying paper [8] is revealed the fact that not only aliphatic acid chlorides containing more than one atom of chlorine take part in the

[4] T. Zincke, *Ber.*, **6**, 137-139 (1873).
[5] C. Friedel and J. M. Crafts, *Compt. rend.*, **84**, 1392-1394 (1877).
[6] C. Friedel and J. M. Crafts, *Compt. rend.*, **85**, 74-77 (1877).
[7] C. Friedel and J. M. Crafts, *Bull. soc. chim.* (2), **28**, 50 (1877).
[8] C. Friedel and J. M. Crafts, *Compt. rend.*, **84**, 1450-1454 (1877).

reaction, but that arylalkyl chlorides, for example benzyl chloride, react with aromatic hydrocarbon under replacement of halogen. Nuclear halogen, however, could not be replaced, for heating chlorinated benzene with benzene and aluminum chloride did not result in evolution of hydrogen chloride.

Before the end of the year, Friedel and Crafts, in collaboration with Ador,[9] described the use of phosgene in the synthesis of ketones and acids. Slow reaction of phosgene with benzene in presence of aluminum chloride resulted in formation of benzophenone; rapid reaction, however, yielded benzoyl chloride and benzoic acid.

At the December 21, 1877, meeting of the Société chimique de France the reaction of phthaloyl chloride with benzene and aluminum chloride to yield phthalophenone and anthraquinone was described.[10]

The January 14, 1878, meeting of the French Chemical Society was presided over by Friedel. At this meeting it was announced that Friedel and Crafts [11] had found that aluminum chloride catalyzed the air oxidation of benzene to phenol and other oxygen derivatives. Toluene behaved the same way. The decomposition of naphthalene into benzene and an anthracene hydride upon heating with aluminum chloride was noted.

At about the same time [12] the action of sulfur on benzene at 75-80° in the presence of aluminum chloride was reported to result in the formation of thiophenol, diphenyl sulfide, and diphenylene sulfide.

The subject of the paper presented to the Société chimique de France on May 3, 1878, was the isolation of durene from products of the reaction of methyl chloride on benzene and aluminum chloride.

Reports dealing with the action of carbon dioxide and of sulfur dioxide and other acid anhydrides on aromatic hydrocarbons in the presence of aluminum chloride were logical sequences to work which had previously been done on reactions with oxygen or sulfur.[13] The report to the French Chemical Society was presented at its June 7, 1878, meeting—about a year after the first announcement of the now well-known Friedel-Crafts reactions. Here we already have a decided extension of the originally described "action of aluminum chloride on organic chlorides." It had been found that benzoic acid was produced in small quantities upon passing a current of perfectly dry carbon dioxide through a mixture of aluminum chloride and benzene heated to the boiling point. Under like conditions, sulfur dioxide reacted much more energetically, yielding benzenesulfinic acid. The now much used reaction of phthalic anhydride for the production of *o*-aroylbenzoic acids was announced. Acetic anhydride was shown to yield acetophenone with benzene and aluminum chloride.

On July 19, 1878, Friedel and Crafts [14] reported results of an investi-

[9] C. Friedel, J. M. Crafts, and E. Ador, *Ber.*, 10, 1854-1858 (1877); *Compt. rend.*, 85, 673-676 (1877).
[10] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2)*, 29, 49 (1878).
[11] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2)*, 29, 99 (1878).
[12] C. Friedel and J. M. Crafts, *Compt. rend.*, 86, 884-887 (1878).
[13] C. Friedel and J. M. Crafts, *Compt. rend.*, 86, 1368-1371 (1878); *Bull. soc. chim. (2)*, 30, 1 (1878).
[14] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2)*, 30, 146 (1878).

gation of the catalytic activity of other metal chlorides on the reaction of benzyl chloride with benzene. The chlorides of zinc, iron, and cobalt were weaker catalysts, but zirconium chloride was as effective as aluminum chloride.

At the November 15, 1878, meeting of the Société chimique de France, Friedel and Crafts[15] reported that upon fusing a mixture of aniline hydrochloride, aluminum chloride, and methyl chloride, a small quantity of a base, probably *o*-toluidine, was obtained.

In 1879, the reaction of benzoyl chloride with durene in the presence of aluminum chloride was reported to result in mono- and di-acylation. The diketone was also prepared by acylation of the monobenzoyldurene.[16]

The reaction of methyl chloride with toluene was extensively studied in 1880. Tetra-, penta-, and hexamethylbenzenes were prepared.[17]

In 1881, several of the previously announced reactions were more thoroughly investigated. A detailed account of the reaction of phthalic anhydride with benzene and benzene homologs was given.[18]

At the December 23, 1881, meeting of the Société chimique de France, Friedel and Crafts commented[19] on a note, published by Gustavson in the *Berichte der deutschen Gesellschaft,* on the decomposing action of aluminum chloride on petroleum hydrocarbons. As has been mentioned, Friedel and Crafts had noted in their first paper the evolution of gas and the formation of condensation products, and a few months later had reported the decomposing action of aluminum chloride on naphthalene. Friedel and Crafts now described the decomposition of hexamethylbenzene to durene and other methylated benzenes as well as the decomposition of triphenylmethane to diphenylmethane.

The condensation of carbon tetrachloride with benzene in the presence of aluminum chloride was restudied, and a report of the results given at the May 27, 1881, meeting of Société chimique de France. It was stated that the reaction proceeded through intermediate formation of diphenylmethane dichloride and triphenylmethane chloride, which upon hydrolysis were converted into benzophenone and triphenyl carbinol, respectively.[20]

A new reaction described in that year[21] was that of ethylene dibromide with toluene and aluminum chloride to yield ditolylethane.

The following year, the use of chloroform and of benzyl chloride in Friedel-Crafts reactions was again studied. Since the original announcement of the formation of triphenylmethane by reaction of chloroform with benzene and aluminum chloride, other investigators had worked on the reaction * and the present paper gives a detailed account of procedure and yields.[22]

[15] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2),* 30, 531 (1878).
[16] C. Friedel, J. M. Crafts, and E. Ador, *Compt. rend.,* 88, 880-884 (1879).
[17] C. Friedel and J. M. Crafts, *Compt. rend.,* 91, 257-260 (1880).
[18] C. Friedel and J. M. Crafts, *Compt. rend.,* 92, 838-837 (1881).
[19] C. Friedel and J. M. Crafts, *Bull. soc. chim.,* 37, 49 (1882).
[20] C. Friedel and C. Vincent, *Bull. soc chim. (2),* 36, 1 (1881).
[21] C. Friedel and M. Balsohn, *Bull. soc. chim. (2),* 35, 52-54 (1881).
* See Chapter 5.
[22] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2),* 37, 6-11 (1882).

At the May 12, 1882, meeting of the Société chimique de France [23] it was noted that the manner of addition of components is a prime factor in the Friedel-Crafts reaction of benzyl chloride with toluene. The production of anthracene as a reaction product was noted.

The next year was uneventful. In 1884, however, Friedel and Crafts [24] gave us an eighty-page review of the reactions of organic chlorides with aromatic hydrocarbons, citing not only their own work but also that of other investigators. New reactions which had been announced by others since 1877 included that of unsaturated acid chlorides with aromatic hydrocarbons,* and of chloropicrin with benzene or phenol to yield triphenylmethane and aurin, respectively.†

The reaction of methylene chloride with toluene and benzene was also reported in 1884.[25] At the December 26, 1884, meeting of the Société chimique de France, the autocondensation of benzyl chloride to give a polymeric substance was described.[26]

In 1885, the decomposing action of aluminum chloride was investigated, and a theory of concomitant hydrogenation and dehydrogenation was advanced.[27] That same year a method for the separation of mixtures of the three xylenes and ethylbenzene formed by the action of aluminum chloride on toluene was described.[28]

A thorough account of the reaction of methylene chloride with benzene or methylbenzenes was given in 1887.[29] The complexities of the reaction are appreciated, and an attempt was made to explain the decomposing and migrating action of aluminum chloride. Thus, the production of toluene and anthracene as well as the expected diphenylmethane in the reaction of methylene chloride with benzene was explained by primary formation of hydranthracene which, upon reduction by the methylene chloride, was converted to anthracene. The methyl chloride thus produced reacted with benzene to yield toluene. The reaction was similarly studied with toluene, *m*-xylene, and pseudocumene.

The second comprehensive review [30] of reactions effected in presence of aluminum chloride appeared in 1888. This is, in effect, a continuation of the 1884 review in which the reactions discussed were limited to those effected with organic chlorides. In the second review, only reactions in which no halogenated component is used are noted. These include those effected with aromatic hydrocarbons and oxygen, sulfur, carbon dioxide, sulfur dioxide, and acid anhydrides. Alkylation with olefins is discussed. Arguments are given to support the view that Friedel-Crafts reactions proceed through primary formation of a complex of the catalyst with aromatic hydrocarbons, that with benzene being $C_6H_6.Al_2Cl_6$.

[23] C. Friedel, *Bull. soc. chim. (2)*, 37, 530 (1882)
[24] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 1, 449-532 (1884).
* See Chapter 6.
† See Chapter 5.
[25] C. Friedel and J. M. Crafts, *Bull. soc. chim.*, 41, 322-327 (1884).
[26] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2)*, 43, 53 (1885).
[27] C. Friedel and J. M. Crafts, *Compt. rend.*, 100, 692-698 (1885).
[28] C. Friedel and J. M. Crafts, *Compt. rend.*, 101, 1218-1223 (1885).
[29] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 11, 263-277 (1887).
[30] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 14, 433-472 (1888).

Friedel's last paper [31] on reactions with aluminum chloride deals with the decomposition of a normal saturated hydrocarbon by aluminum chloride. *n*-Hexane was shown to yield pentane, butane, and propane and a polymeric, brownish, viscous liquid.

[31] C. Friedel and A. Gorgeu, *Compt. rend.*, 127, 590-594 (1898).

Chapter 3

Physical Properties of Anhydrous Aluminum Chloride

Although this book deals primarily with the role of aluminum chloride in organic chemistry, the interest which has been displayed in elucidating the mechanism of Friedel-Crafts and other reactions catalyzed by aluminum chloride necessitates a consideration of the physical properties of the catalyst. Since the catalytic activity of aluminum chloride and similarly reacting catalysts is very probably due to the presence of an incomplete octet, a review of information concerning the molecular structure of aluminum chloride is given in this chapter. Obviously, data concerning physical constants of the salt, its electrical properties, solubility in nonaqueous solvents, and electrical conductivity in such solvents comprise tools which we need, not only for a study of the mechanism of the reactions which are induced by it, but also for arriving at optimum conditions necessary for such reactions. The tendency of aluminum chloride to form complexes with numerous organic and inorganic compounds likewise has a decided effect on the rate of many organic reactions; a summary of such complexes is, therefore, included at the end of this chapter.

An attempt to correlate the physical properties of aluminum chloride with its catalytic activity is made here.

Molecular Structure

Anhydrous aluminum chloride has been observed to crystallize in colorless pseudo-hexagonal plates,[1] composed of three individuals twinned together with rhombic symmetry. The extinction angles were found to be 120° apart. The apparent angle of the optic axes in air was observed to be about 12°. The crystals were optically negative.

The structure of anhydrous aluminum chloride, purified by repeated sublimation under high vacuum, has been worked out in detail by Ketelaar.[2] An earlier structure analysis,[3] based on the Debye-Hull powder method alone and indicating a hexagonal structure, was shown to be incorrect. Optical study showed the six-sided plates to consist of monoclinic pseudo-rhombohedral individuals. In convergent polarized light a biaxial figure was observed. The double refraction was found to be negative, and the angle between the optic axes is about 4° in air. By x-ray examination of single crystals the monoclinic unit cell was observed to

[1] F. Wohler, *Pogg. Ann.*, 11, 146 (1827). H. St. C. Deville and L. Troost, *Compt. rend.*, 45, 821 (1857).
[2] J. A. A. Ketelaar, *Z. Krist.*, 90, 237-255 (1935); *C. A.*, 29, 6812.
[3] W. E. Lashkarev, *Z. anorg. allgem. Chem.*, 193, 270-276 (1930); *C.* 1, 25, 654.

have the dimensions $a = 5.91 \pm 0.02$ Å, $b = 10.24 \pm 0.04$ Å, $c = 6.16 \pm 0.02$ Å, $\beta = 71° 21' \pm 3'$, $Z = 4$. The space group is $C_2^3 - C2$. The structure can also be referred to a pseudo-hexagonal unit cell with $a = 5.91 \pm 0.02$ Å, $c = 17.52 \pm 0.03$ Å, $c/a = 2.97$, $Z = 6$, with the space group $D_3^3 - H3_121$ (or $D_3^5 H3_22$). The chlorine atoms have a close-packed arrangement with rhombohedral symmetry. The aluminum atoms occur in pairs (Al-Al = 0.64 Å) surrounded by six chlorine atoms, thus forming a distinct Al_2Cl_6 grouping within the crystal. The theoretical density calculated from the x-ray data is 2.49.

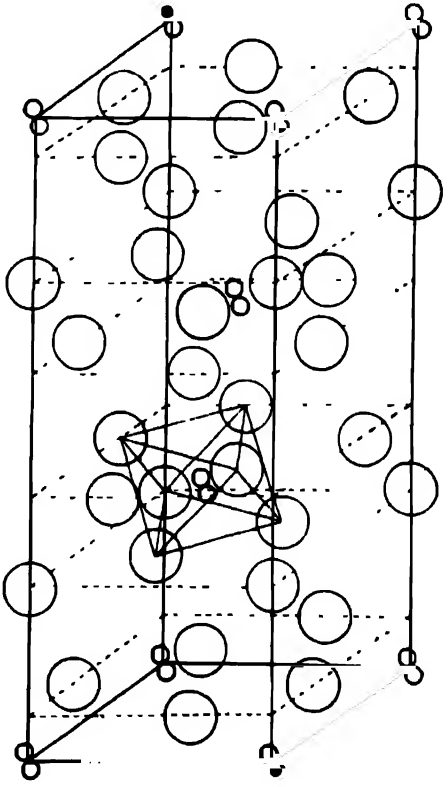


FIG. 1.

Schematic drawing of the structure of Aluminum Chloride. Small circles: aluminum Large circles: chlorine. [J. A A. Ketelaar, *Z. Krist*, 90, 237-255 (1935).]

Further crystal structure study has been made by Wooster,[4] who suggests that anhydrous aluminum chloride may exist in two forms: (1) a yellow modification, which is trigonal and isomorphous with chromic chloride, and (2) the white form, which may be triclinic and is pseudo-trigonal. No corroborative data have yet been published.

The density of crystalline anhydrous aluminum chloride was first determined by Biltz[5] to be 2.41. Later he found that this value was influenced by a partial solubility of aluminum chloride in the pycnometer

[4] N. Wooster *Z. Krist (A)*, 90, 562 (1935); *C. Z.*, 1935, II, 1662
[5] W. Biltz, *Z. anorg. Chem.*, 115, 241-252 (1921); *J. Chem. Soc. Abs.*, 120 (II), 437 (1921).

liquid. Using toluene, in which aluminum chloride is insoluble, he found $d_2^{25} = 2.44$, and the molecular volume to be 54.7.[6] A still later determination of the density [7] showed a value of $d = 2\,465$, which compares favorably with the x-ray determined value of 2.49.

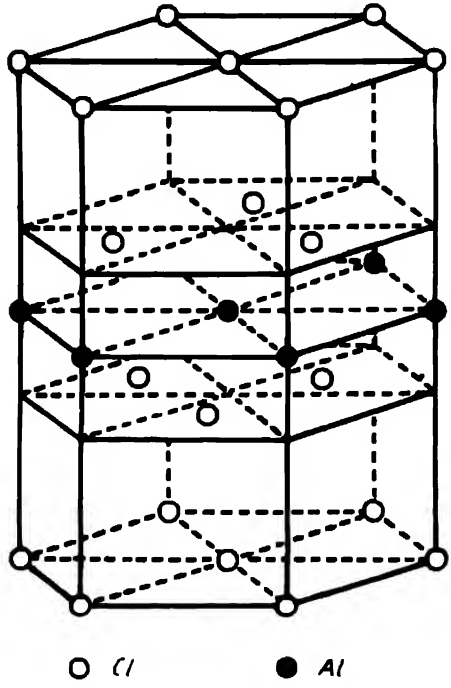


FIG. 2.

Schematic diagram of aluminum chloride. Solid circles aluminum. Open circles: chlorine. [W. E. Laschkarew, *Z. anorg. allgem. Chem.*, 193, 270-276 (1930).]

Evidence in addition to the crystal structure analysis points to existence of aluminum chloride as the double molecule, Al_2Cl_6. This assumption is based on the fact that a linear relationship exists in the physical constants of all other halides, whereas those of the aluminum halides exhibit abnormalities.[8]

Schematic formulas are an aid in interpreting the properties of substances, and what is said here may be instrumental in explaining some of the more complex associated compounds of aluminum chloride, their formation, and subsequent reactions.

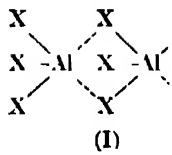
Werner [9] has proposed the following structural formulas for the constitution of aluminum halides:

[6] W. Biltz and W. Wein, *Z. anorg. Chem.*, 121, 257-265 (1922). *J. Chem. Soc. Abs.*, 122 (II), 505 (1922).

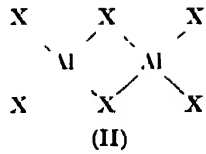
[7] W. Biltz and O. Holsmann, *Z. anorg. allgem. Chem.*, 207, 371-8 (1932). *C. A.* 26, 5800.

[8] W. Biltz and W. Wein, *loc. cit.*

[9] A. Werner, "Neuere Anschauungen auf dem gebiete der anorganischen Chemie," p. 99, bearbeitet von P. Pfeiffer, 5 aufl., Braunschwig, 1923.



(I)



(II)

Vapor density determinations show that the highest associated compound is the dimer, Al_2Cl_6. Formula (II) is the more obvious schematic formula [10] since it is discontinuous, whereas formula (I) can be continuous.[11]

Dipole moment measurements in organic solvents indicate that a dimer is present, which substantiates formula (II) as the structure of aluminum chloride in these solutions.[12]

The chlorine atoms of aluminum chloride do not all have the same reaction value. The two middle chlorines in formula (II) are partly screened off, whereas the other four chlorine atoms are not screened at all. The aluminum atoms are completely screened.[13]

The organic complexes of the aluminum halides behave differently in different solvents. From a study of these behaviors Fischer and Taurinsch [14] assign formula (II) to the concentrated solution of the complexes of aluminum bromide with 3 and 4 associated molecules of benzoazophenone in benzene; and formula (I) to their solutions in carbon disulfide. In ether solution the bromide is symmetrical according to formula (II), and the chloride is given formula (I).

The hypothesis of formula (I) is discussed by Madelung.[15] Older constitutional formulas are discussed by various workers.[16]

In the solid state the physical properties of aluminum chloride do not fall into linear relationship with the bromide and iodide because [17]

(1) The melting point lies between that of the bromide and iodide.
(2) The heat of fusion, in contrast to the bromide and iodide, is much greater.
(3) The cubic expansion coefficient is small.
(4) The LeChatelier-Forcrand quotient of sublimation heat over absolute sublimation temperature is 60 points abnormally high.
(5) It is an electric conductor, whereas the bromide and iodide are insulators.
(6) It has an ionic stratified lattice, the others a molecular lattice.

The bimolecular chloride is not a single ion but is built up of Al^{+++}

[10] H. Hansen, *Z. phys. Chem.*, **8B**, 1-26 (1930); J. A. M. van Liempt, *Rec. trav. chim.*, **51**, 1131 (1932).
[11] W. Fischer and O. Rahlfs, *Z. anorg. Chem.*, **205**, 32 (1932)
[12] H. Ulich and W. Nespital, *Z elektrochem*, **37**, 561 (1931). K. Fajans, *Z. elektrochem.*, **34**, 510 (footnote) (1928).
[13] J. A. M. van Liempt, *Rec. trav. chim.*, **51**, 1132 (1932)
[14] W. M. Fischer and A. Taurinsch, *Z anorg. Chem*, **205**, 310-311 (1932).
[15] W. Madelung, *Ann.*, **427**, 53 (footnote) (1922).
[16] J. F. Heyes, *Phil. Mag. (5)*, **25**, 297 (1888). J. F. Heyes, *Jahresberichte*, **80**, (1888). G. H. Coops, *Chem. Weekblad*, **7**, 531 (1910). W. P. Jorissen, *Chem. Weekblad*, **7**, 1077 (1910)
[17] W. Fischer, *Z. anorg. Chem.*, **200**, 332 (1931).

and $(AlCl_6)^{---}$ ions.[18] Upon melting, the chloride undergoes a constitutional change from an ionic lattice to a molecular bond.[19] The change is not complete, however, because the conductivity of the molten chloride is greater than that of either the bromide or iodide. Also the cubical expansion coefficient is unusually great.[20]

We must expect a similar change when the crystals undergo solution, since in solution the molecules are free to move about one another as in the molten salt. The chloride has a normal Trouton constant, and must be associated in the liquid state as a double molecule, just as in the vapor state.[21] Solid aluminum chloride is likewise bimolecular.[22]

The molecular state of aluminum chloride in the crystalline form differs from that of the molten salt, the molecules in the former being held together by stronger forces; this is shown by its high melting point.

Density

The density of molten aluminum chloride is d^{190} 1.33, d^{200} 1.31, d^{210} 1.28, d^{220} 1.255, d^{230} 1.23; and its molecular volume is 100. The coefficient of thermal expansion of the liquid is therefore 0.002. Biltz and Klemm[23] gave the equation

$$d = 1.32 - 0.0025\,(t - 194)$$

for calculating the density of molten aluminum chloride at any temperature. Dilatometric measurements of aluminum chloride in mercury give the thermal coefficient of cubic expansion, (α), of this salt as 60×10^{-6} at 20-170°.[24] New determinations of the density of aluminum chloride at 17°, −78°, and −183° by a gas-volumetric method give 53.3 for the molecular volume at −273°.[25] The molecular volumes of the molten aluminum halides, near the boiling point, show a linear relationship when plotted against the molecular volumes of the solid potassium halides.[26]

Melting Point

The discovery that anhydrous aluminum chloride can be volatilized without melting was made by Liebig,[27] when he heated small quantities of the material under atmospheric pressure. When large quantities were rapidly heated the salt was found to melt and boil.

The impure salt melts when heated under petroleum, forming a brownish-red liquid which does not dissolve in the oil.[28] In a sealed tube the resublimed salt melts at 193-194°.[29] Friedel and Crafts gave the melting

[18] W. Biltz and A. Voigt, *Z. anorg. Chem.*, 126, 43 (1923). W. Biltz, *Z. anorg. Chem.*, 121, 264 (1922).
[19] W. Fischer, *Z. anorg. Chem.*, 200, 340 (1931).
[20] W. Klemm and E. Tanke, *Z. anorg. Chem.*, 200, 357 (1931).
[21] J. A. M. van Liempt, *Rec. trav. chim.*, 51, 1131 (1932).
[22] W. Biltz, *loc. cit.*
[23] W. Biltz and W. Klemm, *Z. anorg. allgem. Chem.*, 152, 267-294 (1926); *C. A.*, 21, 8
[24] W. Klemm, W. Tilk, and S. V. Mullenheim, *Z. anorg. allgem. Chem.*, 176, 1-22 (1928); *C. A.*, 23, 746.
[25] O. Hulsmann and W. Biltz, *Z. anorg. Chem.*, 207, 371-376 (1932); *C. A.*, 26, 5800
[26] W. Biltz and A. Voigt, *Z. anorg. Chem.*, 126, 39-53 (1923); *J. Chem. Soc. Abs.*, 124 (II), 324 (1923).
[27] J. von Liebig, *Ann.*, 17, 43-51 (1836).
[28] F. Wohler, *Pogg. Ann.*, 11, 146 (1827).
[29] K. Seubert and W. Pollard, *Ber.*, 24, 2575-2578 (1891).

point as 186-190° at 2.5 atmospheres.[30] Kendall and co-workers[31] obtained a sharp melting point of 190.2°, using carefully purified aluminum chloride.

Boiling Point

According to Liebig[27] the sublimed vapor condenses at 180-185°. Scubert and Pollard[29] found an apparent boiling of the resublimed salt at 175-179°. Friedel and Crafts[30] determined the boiling point at several pressures as follows:

B. p. (°C)	167.8	170.4	171.1	171.9	175.7	182.7	204.2	207.5	213.0
Pressure (mm. Hg)	252.1	311.4	311.6	316.5	430.7	755.4	1703.4	2016.1	2277.5

Critical Temperature

The critical temperature was found by Rotinjanz and Suchodsky[32] to be 629.5°K, the sublimation point 456°K, and the ratio $T_c/T_b = 0.724$. According to Smits and his co-workers[33] the triple point occurs at 192.6°C and 171.5 cm of mercury, and the sublimation point is 180.2°. The log p, $1/T$ relationship has been determined (see Fig. 3). Maier gives the boiling point as 177.8°.[34]

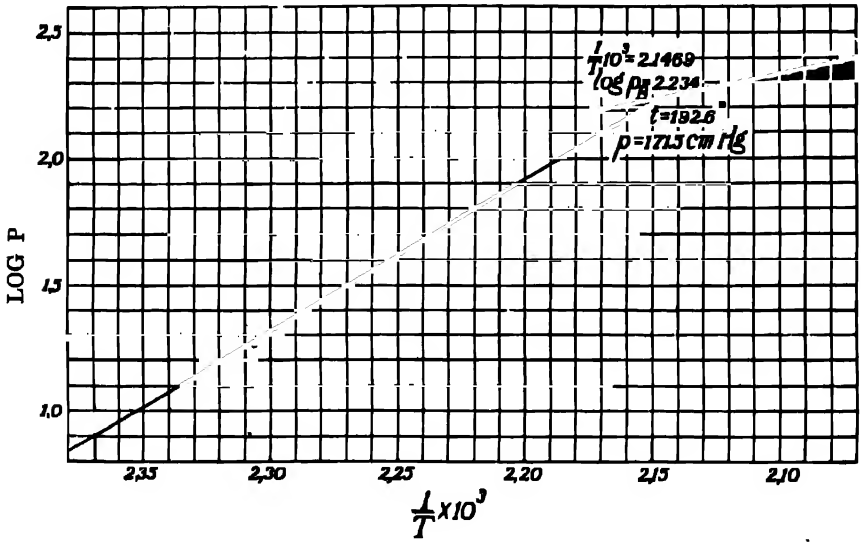


FIG. 3. Triple-point Diagram of Anhydrous Aluminum Chloride
t = °C; T = °K; B = triple point.

[Courtesy A. Smits, J. L. Meyering, and M. A. Kamermans. *Proc. Acad. Sci. Amsterdam*, 35, 195 (1932).]

[30] C. Friedel and J. M. Crafts, *Compt. rend.*, 106, 1764-1770 (1888).
[31] J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Am. Chem. Soc.*, 45, 963-996 (1923); *C. A.*, 17, 1914.
[32] L. Rotinjanz and W. Suchodsky, *Z. physik Chem.*, 87, 635-637 (1914).
[33] A. Smits, J. L. Meyering, and M. A. Kamermans, *Proc. Acad. Sci. Amsterdam*, 35, 193-196 (1932); *C. A.*, 26, 4630.
[34] C. G. Maier, Bureau of Mines Tech. Paper 360, 1-54 (1925); *C. A.*, 20, 2603.

Specific Heat

The specific heat of anhydrous aluminum chloride is 0.188 [35]; the heat of formation of Al_2Cl_6 is 321.87 Calories,[36] and for aluminum chloride, $AlCl_3$, 167 Calories.[37]

Heat of Vaporization

The heat of vaporization given by Maier [34] is 26,380 cal./mole. Smits and his co-workers [38] report that the heat of sublimation is 27,400 calories, the molar heat of fusion is 19,200 gram calories, and the molar heat of vaporization of liquid aluminum chloride is 9600 gram calories. Vapor pressure determination after partial distillation shows that crystalline aluminum chloride behaves as a mixed crystal phase. At higher temperatures a transformation in the direction of inner equilibrium is observed, and above the triple point a rapid establishment of inner equilibrium takes place. These investigators base their values on the vapor-temperature curve for aluminum chloride. In his determination of the heat content of aluminum chloride, however, Fischer [39] states that a linear relationship can be used only for liquid aluminum chloride, but not for the salt in its solid state. He reports 8.5 Calories as the molar heat of fusion.

Vapor Density

The vapor density of aluminum chloride at 350° and at 440° has been determined to be 9.34; the calculated value for Al_2Cl_6 is 9.25.[40] Between 218° and 432° the value is 9.19.[30] At 350-600° the double molecule is the highest polymer present at 10 mm and at 700 mm.[41] Nilson and Pettersson [42] report that at more elevated temperatures there is evidence of dissociation since 4.802 vapor density was found at 758°, dissociation being complete at 800°. The values found at 835° and 943° were 4.542 and 4.557 respectively, corresponding to the molecular formula, $AlCl_3$, whose theoretical vapor density is 4.6. Above 1100° decomposition begins as shown by the following:

Temperature (°C)	218	350	432	440	758	835	943	1117	1244	1260
Vapor density	9.19	9.34	9.19	9.34	4.802	4.542	4.557	4.269	4.247	4.277

Meyer and Zublin,[43] however, state that it is partially dissociated above 100°.

Molecular Weight

Whether the molecular weight of aluminum chloride corresponds to $AlCl_3$ or Al_2Cl_6 has been the subject of some controversy. Friedel

[35] E. Baud, *Ann. chim. phys. (8)*, 1, 8 (1904).
[36] J. Thomsen, *J. prakt. Chem. (2)*, 11, 223, 283 (1875); 12, 85, 271 (1875).
[37] W. Klemm and co-workers, *Z. anorg. allgem. Chem.*, 200, 343-366 (1931); *C. A.*, 26, 1837-1838.
[38] A. Smits, J. L. Meyering, and M. A. Kamermans, *loc. cit.*; *Proc. Acad. Sci. Amsterdam*, 34, 1327 (1931).
[39] W. Fischer, *Z. anorg. allgem. Chem.*, 200, 332-342 (1931); *C. A.*, 26, 365.
[40] J. St. C. Deville and L. Troost, *Compt. rend.*, 45, 821 (1857).
[41] W. Fischer, O. Rahlfs, and B. Benze, *Z. anorg. allgem. Chem.*, 205, 1-41 (1932); *C. A.*, 26, 5247.
[42] L. F. Nilson and O. Pettersson, *Z. physik. Chem.*, 1, 450-464 (1887).
[43] V. Meyer and H. Zublin, *Ber.*, 13, 811-815 (1880).

and Crafts [44] point out that the values obtained by Nilson and Pettersson [42] were in error since they were obtained by Victor Meyer's method. This method is exact only when there is no diffusion of the vapor into the air in the apparatus. At high temperatures, when the volatilization is very rapid, projection and diffusion must take place to a considerable extent, followed immediately afterward by condensation in the cooled stem of the apparatus. Using the Dumas method, Friedel and Crafts redetermined the vapor density of aluminum chloride, taking special care to keep the compound perfectly anhydrous. Their values, at the temperature intervals 218°, 263°, 306°, 357°, 390°, 398°, 400°, 415°, 429°, and 433°, agree closely with the value 9.24 calculated from the formula Al_2Cl_6 and confirm the earlier results of Deville and Troost.[45] The lower values for vapor density obtained at higher temperature by Nilson and Pettersson [42] may be due either to the dissociation $Al_2Cl_6 \rightleftarrows 2AlCl_3$, analogous to the dissociation of iodine, or to the decomposition $Al_2Cl_6 \rightleftarrows Al_2Cl_4 + Cl_2$, as in the case of ferric chloride.

Roux and Louise [46] say that the reason why Nilson and Pettersson never obtained a density corresponding to Al_2Cl_6 for aluminum chloride is that they started with a temperature of 440°, which is far above its boiling point. Aluminum chloride becomes a perfect gas at 218°, 35° above its boiling point, and its vapor density shows no sensible variation between 218° and 400°. It may be concluded [44] that aluminum chloride has the formula Al_2Cl_6 up to 400°.

Werner [47] found that in pyridine solution the molecular weight corresponds to $AlCl_3$, and Beckmann obtained similar results using an ether solution.[48] The formation of addition products with pyridine and nitrobenzene vitiates the molecular weight determinations in these solvents unless precautions are taken to correct the results.[49]

According to Biltz,[50] the boiling point of the aqueous solution agrees with the assumption that the molecules are associated to not less than Al_2Cl_6; but Kohler [49] has shown that in water solution, or in any solvent that is known to combine with it, aluminum chloride has a molecular weight corresponding to the formula $AlCl_3$, whereas in an indifferent solvent like carbon disulfide, it has the doubled molecular weight.

By the boiling point elevation method Coops [51] used concentrations of aluminum chloride varying between 5.79 and 13.75 per cent in alcohol, and found the molecular weight to vary between 243 and 382, the mean of six determinations with different concentrations being 271.3. He concludes that the molecular weight is 267, corresponding to the formula Al_2Cl_6, and assumes that the aluminum atoms are united by a single linking.

[44] C. Friedel and J. M. Crafts, *Compt. rend.*, 106, 1764-1770 (1888); *J. Chem. Soc. Abs.*, 54, 1040
[45] H. St. C. Deville and L. Troost, *Compt. rend.* 45, 821 (1857).
[46] L. Roux and E. Louise, *Bull. soc. chim.*, 50, (2), 497-516 (1888); *J. Chem. Soc. Abs.*, 56, 757 (1889)
[47] A. Werner, *Z. anorg. Chem.*, 15, 1-41 (1897)
[48] E. Beckmann, *Z. physik. Chem.*, 46, 860 (1903)
[49] E. P. Kohler, *Am. Chem. J.*, 24, 385 (1900)
[50] W. Biltz, *Z. physik. Chem.*, 40, 185-221 (1902), *J. Chem. Soc. Abs. (II)*, 310 (1902)
[51] G. H. Coops, *Chem. Weekblad*, 7, 345-351 (1910), *J. Chem. Soc. Abs.*, 98 (II), 506 (1910).

Olivier [52] considers Coops' results untrustworthy, and attributes them to the use of a hydrated aluminum chloride. According to him, Coops has advanced no evidence in favor of the formula Al_2Cl_6.

Ulich,[53] studied the molecular weight of aluminum chloride and its complexes by freezing point and boiling point measurements in several solvents, including benzene, carbon disulfide, diethyl ether, nitrobenzene, diphenyl ketone, and acetyl chloride. Special precautions were taken to keep out traces of moisture. At great dilution the molecular size was that of the simple molecule; with increasing concentrations the salts showed strong association, in some cases exceeding double the molecular weight. Beckmann [48] has reported that the molecular weight in diethyl ether corresponds to the formula $AlCl_3$.

It may be concluded that the molecular state of anhydrous aluminum chloride is the dimer, Al_2Cl_6, when solid, liquid, or gas below 440°. At temperatures between 440° and 800° a mixture of the dimer and monomer is in equilibrium. Only the monomer exists between 800° and 1000°. Above 1000° the monomer is somewhat dissociated. The dimeric state occurs in solution if indifferent solvents, such as carbon disulfide, are used. In solvents that are known to combine with it, such as water, pyridine, nitrobenzene, and diethyl ether, anhydrous aluminum chloride exists only as a complex with the solvent. The molecular state of the aluminum chloride in this complex is usually the monomer in dilute solution, but at increasing concentrations dimeric association occurs.

Optical Studies

Jevons [54] notes that active nitrogen excites phosphorescence in aluminum chloride. Krepelka [55] observed a bright green phosphorescence when aluminum chloride, freshly prepared from aluminum and chlorine in a tube through which nitrogen had been passed, was gradually cooled in nitrogen. He ascribes the phenomenon to the activation of some of the nitrogen by the violent reaction of the chlorine left in the tube with the aluminum.

The band spectrum of the uncondensed discharge through aluminum chloride has been studied, and a characteristic group of bands near wave length 2610 A being shaded toward the red has been found.[56]

It was determined by use of a sector photometer designed by Lewis in conjunction with a quartz spectrograph, that the ultraviolet absorption band of aluminum chloride in aqueous solution has its head near 2730 A.[57]

Bhaduri and Fowler [58] studied the emission spectrum of aluminum chloride at high dispersion, using vacuum tubes with aluminum electrodes. They report a band system extending from 2555 to 2810 A with

[52] S. C. J. Olivier, *Chem. Weekblad*, 7, 378 (1910); *J. Chem. Soc. Abs. (II)*, 507 (1910). G. H. Coops, *Chem. Weekblad*, 7, 1071-1076 (1910); *J. Chem. Soc. Abs*, 100 (II), 116 (1911).
[53] I. H. Ulich, *Z. physik. Chem. (Bodenstein-Festband)*, 423-431 (1931); *C. A.*, 26, 898.
[54] W. Jevons, *Nature*, 111, 705-706 (1923).
[55] H. Krepelka, *Nature*, 112, 134 (1923).
[56] W. Jevons, *Proc. Roy. Soc. London*, 106A, 174-194 (1924).
[57] F. H. Getman, *J. phys. Chem.*, 29, 853-864 (1925); *C. A.*, 19, 3210.
[58] B. N. Bhaduri and A. Fowler, *Proc. Roy. Soc. London*, 145A, 321-336 (1934); *Brit. Chem. Abstracts* A, 828 (1934).

its greatest intensity at 2610 Å. Most of the bands are degraded toward the red, but there are two strong short sequences of bands of the same system which are shaded in the opposite direction. The heads of the bands occur in pairs which have been interpreted as representing R and Q branches. The main bands due to the molecules $AlCl^{35}$ are associated with bands due to $AlCl^{37}$.

Mahanti made measurements on greatly dispersed bands in the spectrum of aluminum chloride. He says the vibrational levels could be analyzed.[59]

Bredig and Koch [60] measured the refraction and dispersion of gaseous aluminum chloride in the visible region at temperatures from 230-300°. They discuss an arrangement for reducing vibrations in the interferometer used, and conclude that a decrease in refraction increases with increasing deformability of halide ion.

In a study of the relation between absorptive spectra of metallic ions in aqueous solution and their valence, Crymble [61] found that metals possessing only one valence are non-absorptive down to a wave-length of 2350 Å when using a 10-mm layer of the molar solution of the metal, whereas metals possessing more than one valence absorb in this region. An aluminum chloride solution belongs in the non-absorption class, although it has a slight absorption between wave-lengths 2500 and 2350 Å.

Aqueous solutions of several metallic chlorides, including aluminum chloride, absorb light selectively; the wave-length corresponds to the head of the absorption band of each salt, being approximately 2730 Å. The presence of this characteristic absorption band throughout a series of chlorides was shown to be due to the metal and not to the common ion. Absorption does not follow Beer's law. The calculated molecular extinction coefficients increase with the atomic weight of the combined metal.[62]

The molar refractivity of aluminum chloride in nitrobenzene solution differs from that found in water and from that of the solid salts, suggesting formation of complexes with the solvent. Corresponding differences are found when other non-aqueous solvents are used.[63] Emission of positive ions by aluminum chloride occurs only below 450°.[64]

Conductivity of Anhydrous Aluminum Chloride

Schmidt [65] found that the vapors of aluminum halides are electrical conductors, and that the conductivity increases rapidly with rising temperature. At low potentials the current through the vapor is proportional to the applied voltage, reaching a saturation current at a sufficiently high applied voltage. When still higher potentials are applied, collision ionization occurs, and this stage is succeeded by luminous discharges.

[59] P. C. Mahanti, *Z. physik.*, **88**, 550-559 (1934); *C. A.* **28**, 3334
[60] M. A. Bredig and F. K. V. Koch, *Z. physik. Chem.*, **B24**, 103-154 (1934); *C. A.*, **28**, 2585.
[61] C. R. Crymble, *J. Chem. Soc.*, 101, 266-273 (1912).
[62] F. H. Getman, *J. Phys. Chem.*, **29**, 853-864 (1925).
[63] V. A. Plotnikov and I. M. Podorvan, *Mem. Inst. Chem. Ukrain. Acad. Sci.*, **3**, 159-166 (1936); *C. A.*, **31**, 6084.
[64] O. Gossmann, *Z. Physik.*, **22**, 273-274 (1924); *J. Chem. Soc. Abs*, **126** (II), 292 (1924).
[65] G. C. Schmidt, *Ann. physik. (4)*, **35**, 401-443 (1911); *J. Chem. Soc Abs.*, **100** *(II)*, 788 (1911).

Bryan [66] measured the conductivity of flames charged with aluminum chloride. Wöhler and Buff [67] stated that fused anhydrous aluminum chloride can be electrolyzed. Hampe [68] stated that, if quite pure, the molten salt does not conduct electricity.

In the case of solid and molten aluminum chloride Biltz and Voigt [69] found the electrical conductivity of crystalline aluminum chloride to increase with temperature from a zero value at room temperature to a maximum at the melting point. On melting, the conductivity drops abruptly to zero, and slowly rises upon increasing the temperature of the molten salt. From this behavior they conclude that in the crystals of aluminum chloride an ion lattice exists, the ions being Al^{+++} and $(AlCl_6)^{-}$, which combine on melting so that the melt consists almost entirely of the molecules, Al_2Cl_6. Their results are tabulated as follows:

(Text cont'd on p. 26)

	$AlCl_3$ (m p. 190-195°)	
Temp. (°C)	Specific Conductivity ($\times 10^{-6}$)	Equivalent Conductivity ($\times 10^{-6}$)
146	0.29	..
164	0.7	..
189	2.6-5.0	..
194 (m.p.)	0.45	15
200	0.56	19
209	0.66	23
218	0.76	27
227	0.86	31
236	0.96	35
245	1.1	41

Klemm [70] found a specific conductivity of 0.45×10^{-6} mho at the melting point; and he reported that the absolute temperature coefficient of equivalent conductivity is 0.5×10^{-6} mho.

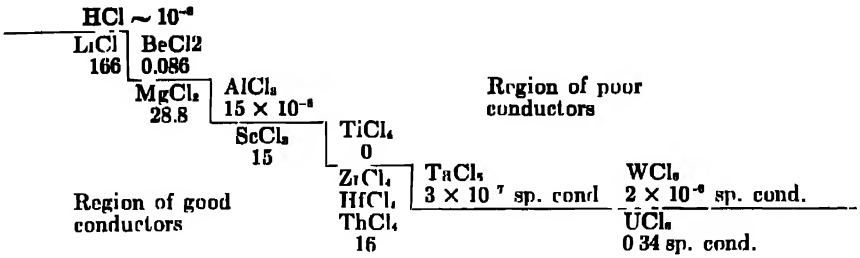
Biltz and Klemm [71] point out that solid aluminum chloride has a negative temperature coefficient of conductivity, and attribute this to a repression of ionization. Molten aluminum chloride consists essentially of molecules; and crystalline aluminum chloride contains an appreciable quantity of auto complex ions. Their equation for the equivalent conductivity of molten aluminum chloride at any given temperature is

$$\frac{\mu}{3} = 15 \times 10^{-6} + 0.5 \times 10^{-6} \ (t - 194)$$

In their study of the equivalent conductivity of the halides of the elements, the equivalent conductivities at their melting points were taken as the basis of comparison of the different salts. If these conductivities are plotted against temperature, the halides of the main groups of the periodic system will fall in the region of high temperature and high conductivity; the halides of the minor groups occupy an intermediate posi-

[66] A. B. Bryan, *Phys. Rev. (2)*, 18, 275-291 (1921).
[67] F. Wöhler and H. Buff, *Ann.*, 103, 218-229 (1857). H. Buff, *Ann.*, 110, 257-288 (1859).
[68] W. Hampe, *Chem. Ztg.*, 11, 54, 934 (1887); *J. Chem. Soc. Abs.*, 54, 211 (1888).
[69] W. Biltz and A. Voigt, *Z. anorg. Chem.*, 126, 39-53 (1923); *J. Chem. Soc. Abs.*, 124 (II), 324 (1923).
[70] W. Klemm, *Z. anorg. allgem. Chem.*, 152, 252-266 (1926).
[71] W. Biltz and W. Klemm, *Z. anorg. allgem. Chem.*, 152, 267-294 (1926); *C. A.*, 21, 6.

tion; and the halides of the unsaturated compounds come in the region of low temperature and low conductivity. A diagonal, step-wise line across the periodic table separates the good from the poor conductors as follows:



The lower chloride of a metal conducts better than a higher chloride of the same metal. Good conductors have high melting points; their melting is termed ionic fusion. That of the others is termed molecular fusion, although the ionizations and mobilities vary from one extreme to the other.

Klemm and co-workers,[72] in a study of the aluminum halide ammoniates, found that the conductivity coefficient indicates that the salts, when melted, are intermediate between the molecular and the ionic

$AlCl_3.NH_3$ (solid)	
Temp. (°C)	Spec. Cond. (× 10^{-2})
136	1.43
161	2.03
175	2.37
178	2.46

states. The conductivity of the halides compares as follows: $AlCl_3.NH_3 > AlBr_3.NH_3 > AlI_3.NH_3$.

Izbekov and Tschovnik[73] measured the decomposition potentials of metallic chlorides in fused aluminum chloride and in $AlCl_3$-KCl as solvents. The decomposition potentials of chlorides in both solvents of the metals investigated were found to be in the decreasing order, aluminum, cadmium, silver, antimony, tin, and bismuth. They[74] also found that the decomposition potential of a fused halide is scarcely changed by the addition of another halide of the same metal. However, the decomposition potentials of halides of tin and antimony, and to a smaller extent of bismuth, are altered by the addition of aluminum chloride or aluminum bromide. Mixtures of two halides of the same metal do not conduct if their components are non-conductors; but the system AlX_3-SbX_3 and AlX_3-HgX_2 (X = Cl, Br) are conductors, although their components are not.

[72] W. Klemm, E. Clausen, and H. Jacobi, *Z. anorg. Chem.*, 200, 367-384 (1931).
[73] V. A. Izbekov and N. G. Tschovnik, *Mem. Inst. Chem. Ukrain. Acad. Sci.*, 4, 57-70 (1937); *Brit. Chem. Abstracts* A (I), 520 (1937)
[74] V. A. Izbekov and N. G. Tschovnik, *Mem. Inst. Chem. Ukrain. Acad. Sci.*, 4, 71-83 (1937); *Brit. Chem. Abstracts* A (I), 520 (1937).

Solvents for Aluminum Chloride

Information concerning solubility of aluminum chloride in non-aqueous solvents is summarized in the following table. Rather detailed studies have been made of many non-aqueous solutions of the salt.

(Text cont'd on p. 26)

Table 1. Solubility of Aluminum Chloride in Non-aqueous Solvents.

s = soluble
s.s. = slightly soluble
v.s. = very soluble
m.s. = moderately soluble
i = insoluble

Solvent	Solubility	Nature of Study and Remarks	Ref No.
Carbon disulfide	0.2 g. in 1 liter	.....	45
Carbon disulfide	under 2%	2° temp rise noted; no color change	29
Carbon disulfide	s.s. at b.p.	.....	12, 13
Chloroform	0.1% at 0°	.....	14
Chloroform	about 10%	boils; no color change	29
Carbon tetrachloride	0.7% at 4°	.....	14
Carbon tetrachloride	under 2%	2° temp. rise; no color change	29
Phosgene	s	.....	15
Phosgene	55% at 25°	.....	16
Methyl iodide	s	.....	36
Ethyl chloride	s	.....	36
Ethyl bromide	s	complex formation and conductivity	36
Ethyl iodide	s	.....	36
Ethylene dichloride	under 4%	3° temp. rise; pale straw color	29
asym.-Tetrachloroethane	.....	.....	46
n-Propyl chloride	s	conductivity	26
Isopropyl chloride	s	conductivity	26
n-Propyl iodide	s	.....	36
Butyl chloride	s	conductivity	37
Isobutyl chloride	s at 0° (decomp.)	conductivity	38
Isobutyl chloride	s	conductivity	37
Amyl chloride	s	conductivity	37
Isoamyl chloride	s	conductivity	37
Hexyl chloride	s	conductivity	37
Cyclohexyl chloride	s	conductivity	26
Ether	s	.....	3, 17, 41
Ether	.5 g. in 1 cc.	boils; dark purple solution	29
Methylal	i	.....	23
Methyl alcohol	.....	boils; white ppt.	29
Ethyl alcohol	v.s.	.....	3
Ethyl alcohol	s (decomp.)	.....	27
Ethyl alcohol	s	.....	28
Ethyl alcohol	s	viscosity of solutions	34
Ethyl alcohol	s	ebullioscopic solvent	35
Ethyl alcohol	.5 g. in 1 cc.	boils; pale yellow color; solidifies	29
Oenanthyl alcohol	s s.	conductivity	39
Diethylene glycol	above 10%	30° temp. rise; colorless solution	29
Acetic acid	13%	pH of solution	18
Ethyl acetate	i	.....	22
"Cellosolve" acetate	above 50%	30° temp. rise	29

Table 1.—*Continued.*

Solvent	Solubility	Nature of Study and Remarks	Ref. No
Acetonitrile	s		19
Acetyl chloride	v.s.		26
Acetone	s	conductivity	39
Acetone	36.5% at 18°	conductivity	17
Methylacetone	s	conductivity	39
Mesityl oxide	s	conductivity	39
Acetaldehyde	s.s.	conductivity	39
Paraldehyde	s.s.	conductivity	39
Valeraldehyde	s.s.	conductivity	39
Crotonaldehyde	s.s.	conductivity	39
Ethyl nitrate	s		24
Nitromethane	3 g. in 5 cc.		29
Halowax	.5 g. in 2 cc.	1° temp. rise; dark purple solution	29
Gasoline	s.s.	6° temp. rise; red color	29
Petroleum ether	s.s.	1° temp. rise; faint yellow color	29
Ligroin	5 g. in 4 cc.	8° temp. rise; very faint yellow tinge	29
Varnoline	s.s.	2° temp. rise; red color	29
Phenylcyclohexane	5 g. in 1 cc.	15° temp rise; red oil after one hour	29
Benzene	0.72% at 80°		30
Benzene	s.s	2° temp. rise; olive green color	29
Benzene			31
Toluene		3° temp. rise; greenish yellow color	29
Toluene	0.92% at 73°		30
Toluene	i	measurement of density of aluminum chloride	40
Amylbenzene	s.s.	3° temp. rise; red, insoluble oil	29
Xylene	s.s.	5° temp. rise; heavy red oil after one hour	29
Bromobenzene	i		31
Chlorobenzene			46
Nitrobenzene	v.s.	.....	31
Nitrobenzene	s	.....	30
Nitrobenzene	s	refraction of $AlCl_3$	42
o-, *p*-, and *m*-Nitrotoluenes	s	.....	30
o-Nitrotoluene	s	.....	26
o-, *p*-, and *m*-Chloronitrobenzenes	s.	.....	30
o-, *p*-, and *m*-Nitrobenzenes	s	.....	30
Benzotrichloride	stable sol. below 40°	.....	25
Benzonitrile	s	.....	20
Benzonitrile	.5 g. in 1 cc.	20° temp. rise; colorless	29
Benzoyl chloride	v.s.	.....	26
Benzoyl chloride	s	.....	33
Acetophenone	s	conductivity	39
Benzophenone	s	.....	32
Benzaldehyde	m.s.	.....	39
Cinnamaldehyde	m.s.	.....	39
Anisole	s	.....	26
Pyridine	s	.....	21
Liquid chlorine	i	.....	1, 2
Liquid chlorine	s	.....	3
Liquid ammonia	i	.....	4

Table 1.—*Concluded.*

Solvent	Solubility	Nature of Study and Remarks	Ref No.
Anhydrous hydrazine	1% at room temp.	.....	11
Liquid phosphine	i	.....	5
Hydrogen fluoride	s (decomp.)	.....	44
Liquid hydrogen sulfide	i	.....	8
Liquid hydrogen sulfide	m.s.	.....	9
Liquid hydrogen sulfide	s.s.	.....	10
Sulfur trioxide	s	ebullioscopic solvent	7
Sulfuryl chloride	s	ebullioscopic solvent and conductivity	7,43
Chromyl chloride	s	ebullioscopic solvent	7
Vanadium oxychloride	i	.....	6

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46. No solubility data available, but this compound has been very frequently used as a diluent in Friedel-Crafts reactions.

Properties of Aluminum Chloride Solutions

In Ethanol

Aluminum chloride has been reported to be easily soluble in ethanol,[75] but according to other investigators[76] the solution occurs only under

[75] O. R. Ralston, *Chem. News*, 127, 247 (1923).
[76] E. Lloyd, C. B. Brown, D. G. R. Bonnell, and W. J. Jones, *J. Chem. Soc.*, 658-666 (1928).

simultaneous decomposition and evolution of hydrogen chloride. The density and conductivity of alcoholic solutions have been determined by Cattaneo.[77]

Viscosity measurements were made by Dolian [78] on solutions of several metallic chlorides in pure and mixed solvents. The relative increase in viscosity of ethyl alcohol solutions of these chlorides is in the order $NiCl_2 > AlCl_3 > CoCl_2 > CuCl_2 > FeCl_3 > CdCl_2 > SnCl_4 > HgCl_2$. Predicted from molecular weights, the relative effect would be smaller for aluminum chloride. This anomalous behavior of aluminum chloride may be explained by its greater power of forming solvates.

In Acetone

The specific electric conductivity in reciprocal ohms of a solution secured by dissolving $3AlCl_3{,}5CH_3COCH_3$ in acetone has been determined at 18° for solutions containing 14.22-36.48 weight per cent of aluminum chloride. Maximum conductivity was secured with solutions containing 1 mole of aluminum chloride in about 10 moles of acetone. Complex soluble compounds were present in solution; upon sufficient dilution these were decomposed into $[Al(CH_3COCH_3)_6]^{+++}$ and Cl' ions.[79]

In Chloroform and Carbon Tetrachloride

Lloyd [80] gives the following data on the solubility of aluminum chloride in carbon tetrachloride and chloroform.

Solubility of $AlCl_3$

Temp. (°C)	CCl_4 (g/l)	$CHCl_3$ (g/l)
−15		0.65
0		1.00
4	0.74	
14	0.22	
20	0.15	
25	...	0.72
34	0.06	

In Phosgene

Vapor tension curves at 0°, 25°, and 250° for aluminum chloride in phosgene solution were prepared by Germann.[81] There is appreciable vapor pressure lowering with increased concentration of aluminum chloride. The data indicated Al_2Cl_6 as the formula for aluminum chloride in phosgene solution.

The densities of solutions of aluminum chloride in liquid phosgene are [82]:

[77] C. Cattaneo, *Atti Accad. Torino*, 28, 627 (1892-3), *Atti Line.* (5), 4, II, 69 (1895).
[78] F. E. Dolian and H. T. Briscoe, *J. Phys. Chem.*, 41, 1129-1138 (1937); *Brit. Chem. Abstracts*-A, (I), 22 (1938).
[79] M. I. Uschakow, *Z. anorg. Chem.*, 183, 144, 147 (1929).
[80] S. J. Lloyd, *J. Phys. Chem.*, 22, 300-303 (1918); *C. A.*, 12, 1433.
[81] A. F. O. Germann and G. H. McIntyre, *J. Phys. Chem.*, 29, 102-105 (1925), *C. A.*, 19, 920.
[82] A. F. O. Germann, *J. Phys. Chem.*, 29, 139-141 (1925); *C. A.*, 19, 1217.

% $AlCl_3$ in phosgene	Densities at 0°C	at 25°C
0.00	1.4275	1.3685
2.97	1.4422	
2.99	.....	1.3861
46.33	1.6473	.....
46.53		1.6089

Electrolysis of phosgene solutions of aluminum chloride yields the products carbon monoxide and chlorine.[83] The specific conductivity of the solvent is 0.7×10^{-8} at 25° and that of the saturated solution of aluminum chloride 0.7×10^{-3}. The volume of products, chlorine and carbon monoxide, collected together, corresponds to 65-70 per cent of the volume calculated by Faraday's law. The author explains this on the grounds that the gases recombine to form phosgene because of the action of light and the catalytic influence of aluminum chloride.[84]

In Aromatic Compounds

According to Menschutkin,[85] the solubility of aluminum chloride in benzene at 17° is 0.12% and at 80° is 0.72%; in toluene it is 0.26% at 17° and 0.92% at 73°. Bruner [86] has reported, however, that aluminum chloride is insoluble in benzene and bromobenzene.

Menschutkin [87] has studied the solubility of aluminum chloride in nitrobenzene and its derivatives, noting the formation of complexes. The

Mole % $AlCl_3$	Crystallization Temp. (°C)	
0.0	5.5	
4.1	4	
9.5	2	(eutectic) $AlCl_3,0.953C_6H_5NO_2$
13.5	10	
16.8	15	
21.1	20	
28.8	25.5	
30.3	35	
32.4	45	
34.7	55	
37.5	65	
41.1	75	
45.9	85	
47.7	88	
50.0	90	(dystectic) $AlCl_3,C_6H_5NO_2$
51.7	88	
53.6	82	
56.0	72	
57.8	62	
59.6	52	(eutectic) $AlCl_3,0.68C_6H_5NO_2$
60.8	70	
62.1	90	
63.8	110	
65.9	130	
70.7	160	
78.7	180	
100.0	194	

[83] A. F. O. Germann, *Science*, 61, 71 (1925); *C. A.*, 19, 765.
[84] A. F. O. Germann, *Science*, 61, 70-71 (1925); *C. A.*, 19, 770.
[85] B. Menschutkin, *J. Russ. Phys.-Chem. Soc.*, 41, 1089-1110 (1909); *C. Z.*, 1910, I, 168.
[86] L. Bruner, *Z. phys. Chem.*, 41, 533 (1902).
[87] B. Menschutkin, *J. Russ. Phys.-Chem. Soc.*, *loc. cit.*; 42, 58-94 (1910); *C. Z.*, 1910, I, 1240-1242.

foregoing crystallization temperatures are given for various concentrations of aluminum chloride in nitrobenzene:

The constants for solutions of aluminum chloride in *o*-chloronitrobenzene are:

Mole % $AlCl_3$	Crystallization Temp. (°C)	
0	32.5	
11.8	27	
18.4	21	
23.1	15	(eutectic) $AlCl_3$,3.33*o*-$C_6H_4Cl.NO_2$
25.8	25	
28.8	35	
31.9	45	
35.2	55	
38.7	65	
42.6	75	
47.4	85	
50.0	89	(dystectic) $AlCl_3$,$C_6H_4ClNO_2$
52.8	85	
55.7	77	
58.5	69	(eutectic) $AlCl_3$,0.71$C_6H_4ClNO_2$
59.7	90	
61.9	110	
64.5	130	
69.0	150	
75.6	170	
77.6	175	

Crystallization diagrams were also prepared for solutions of aluminum chloride, *m*- or *p*-chloronitrobenzene, *o*-, *m*-, and *p*-bromonitrobenzene, and *o*-, *m*-, and *p*-nitrotoluene. Eutectic points are given:

Solvent	Eutectic Point		Addition Compound Formed
	Temp. (°C)	Mole % $AlCl_3$	
m-chloronitrobenzene	36	19.0	$AlCl_3$,4.26*m*-$C_6H_4Cl.NO_2$
"	81	59.8	$AlCl_3$,0.67*m*-$C_6H_4ClNO_2$
" (dystectic)	104	50.0	$AlCl_3$,*m*-$C_6H_4ClNO_2$
p-chloronitrobenzene	68	19.5	$AlCl_3$,4.13*p*-$C_6H_4ClNO_2$
"	94	62.1	$AlCl_3$,0.61*p*-$C_6H_4ClNO_2$
" (dystectic)	126	50.0	$AlCl_3$,*p*-$C_6H_4ClNO_2$
o-bromonitrobenzene	20	24.3	$AlCl_3$,3.1*o*-$C_6H_4BrNO_2$
"	80	41.2	$AlCl_3$,0.77*o*-$C_6H_4BrNO_2$
" (dystectic)	100	58.9	$AlCl_3$,*o*-$C_6H_4BrNO_2$
m-bromonitrobenzene	47	16.9	$AlCl_3$,4.92*m*-$C_6H_4BrNO_2$
"	97	57.6	$AlCl_3$,0.73*m*-$C_6H_4BrNO_2$
" (dystectic)	116	50.0	$AlCl_3$,*m*-$C_6H_4BrNO_2$
p-bromonitrobenzene	99	30.2	$AlCl_3$,2.31-*p*-$C_6H_4BrNO_2$
"	113	62.7	$AlCl_3$,0.59*p*-$C_6H_4BrNO_2$
" (dystectic)	145.	50.0	$AlCl_3$,*p*-$C_6H_4BrNO_2$
o-nitrotoluene	−9.3	1.0	$AlCl_3$,99.0*o*-$C_6H_4CH_3NO_2$
"	45	62.1	$AlCl_3$,0.61*o*-$C_6H_4CH_3NO_2$
" (dystectic)	99.5	50.0	$AlCl_3$,*o*-$C_6H_4CH_3NO_2$
m-nitrotoluene	13	7.9	$AlCl_3$,11.6*m*-$C_6H_4CH_3NO_2$
"	45	62.1	$AlCl_3$,0.61*m*-$C_6H_4CH_3NO_2$
" (dystectic)	99.5	50.0	$AlCl_3$,*m*-$C_6H_4CH_3NO_2$
p-nitrotoluene	37	19.2	$AlCl_3$,4.21*p*-$C_6H_4CH_3NO_2$
"	45	64.6	$AlCl_3$,0.55*p*-$C_6H_4CH_3NO_2$
" (dystectic)	109	50.9	$AlCl_3$,*p*-$C_6H_4CH_3NO_2$

Solubility data on aluminum chloride in benzoyl chloride have been reported [88]:

Weight % $AlCl_3$	Crystallization Temp (°C)	
0	−0.5	
7.9	−4	
12.7	−7.5	(eutectic) $AlCl_3,6.53C_6H_5COCl$
14.1	0	
16.3	10	
18.8	20	
21.6	30	
25.5	40	
28.8	50	
30.0	60	
37.5	70	
42.2	80	
47.1	90	
48.7	93	(dystectic) $AlCl_3,C_6H_5COCl$
50.6	90	
52.9	80	
57.2	60	
61.0	40	

Data on solubility of aluminum chloride in benzophenone follow [89]:

Mole % $AlCl_3$	Crystallization Temp (°C)	
0	48	
11.1	44	
20.0	39.5	(eutectic) $AlCl_3,4.92C_6H_5COC_6H_5$
25.5	60	
29.8	80	
36.3	100	
44.4	120	
46.6	125	
50.0	130	(dystectic) $AlCl_3,C_6H_5COC_6H_5$
53.3	125	
54.5	120	
58.1	100	
60.9	80	
62.2	70	
63.5	60	(eutectic) $AlCl_3,0.57C_6H_5COC_6H_5$
64.2	80	
65.3	100	
66.9	120	
69.9	140	
72.1	150	
74.9	160	
78.4	170	
83.3	180	
87.1	185	
91.7	190	
94.8	192	
100.0	194	

Walker [90] in a study of ionization and chemical combination found that ionization is not the primary factor influencing the Friedel-Crafts reaction. The conductivity of solutions of aluminum chloride in *o*-nitrotoluene and in anisole are compared with their rates of reaction which are indifferent for the nitro- compound and very rapid for the anisole.

[88] B. Menschutkin, *J. Russ. Phys. Chem. Soc.*, 42, 1310-1318 (1910); *C. Z.*, 1911, I, 481.
[89] B. Menschutkin, *Iswiestja de Petersburger Polytechnikums*, 13, 1-16; *C. Z.*, 1910, II, 154.
[90] J. W. Walker, *J. Chem. Soc.*, 85, 1082-1098 (1904).

Molecular Conductivities

In o-nitrotoluene		In anisole	
Volume in liters (V)	Molecular cond. (μ)	V	μ
1.15	0.6	0.31	0.026
2.30	0.8	0.62	0.026
4.60	1.1	0.78	0.023
9.20	1.5	0.99	0.019
18.40	2.2	1.25	0.018
36.80	3.7	1.55	0.012
73.60	4.3	1.97	0.010
147.20	1.9		

Plotnikov and Vaĭsberg [91] have studied the conductivities of aluminum and antimony halides in nitrobenzene solution, finding the solutions to be good conductors. For aluminum chloride in nitrobenzene the specific conductivity passes a maximum. For the ternary system aluminum chloride-antimony bromide-nitrobenzene the specific conductivity is less than when the antimony bromide is omitted. Dilution of the ternary system with nitrobenzene changes the conductivity in the same manner as it would the binary system, aluminum chloride-nitrobenzene. That is, the third component of the system only qualifies the change in conductivity.

The specific conductivity of aluminum chloride is greater in benzene than in nitrobenzene, according to Plotnikov and Gorenbein.[92] It rises with dilution, and with increasing concentrations of added alkali halides.

In Acid- and Alkyl Halides

Ionization is consequent to chemical reaction, as shown in the reaction of benzoyl chloride with anisole, using an anisole solution of aluminum chloride and adding a mole of benzoyl chloride for each mole of aluminum chloride present. Comparing conductivities before and after reaction with $\frac{N}{50}$ KCl solution they found an increase from 1/50 to a conductivity somewhat greater than the value for the standard KCl. The molecular conductivity for the resulting complex of the ketone with aluminum chloride was calculated to be:

V	μ
0.727	2.0
1.142	2.3

Similar results were obtained when benzoyl chloride was replaced by acetyl chloride and thionyl chloride. Considerable conductivity could be detected for solutions of aluminum chloride in methyl iodide, ethyl iodide, *n*-propyl iodide, ethyl bromide, and chloroform. For ethyl bromide solution of aluminum chloride the resistance was least and the following quantitative data were obtained:

[91] V. A. Plotnikov and R. G. Vaĭsberg, *Mem. Inst. Chem. Ukrain. Acad. Sci.*, 3, No. 3, 337-356 (1936); *C. A.*, 31, 5689.
[92] V. A. Plotnikov and E. Ya. Gorenbein, *Mem. Inst. Chem. Ukrain. Acad. Sci.*, 3, 471-487 (1936); *C. A.*, 31, 7764.

V	μ
1.6	0.7
3.2	0.4

Addition of chloroform or carbon tetrachloride to the solution of aluminum chloride in ethyl iodide caused an increase in conductivity as well as chemical reaction. A solution of aluminum chloride in a mixture of ethyl bromide and carbon tetrachloride conducts just as well as when ethyl iodide is used. Chemical action is much slower in this case, however. The facts agree best with the hypothesis of an intermediate compound which undergoes rearrangement to a more stable system, the method of rearrangement depending on a molecular, and not an accidental, ionic dissociation of the complex.

With ethyl bromide as solvent one mole each of aluminum chloride and benzene or naphthalene was added and the molar conductivities determined as based on the aluminum chloride present.

-Benzene-	——Naphthalene——	
V	μ	Color
1	3 9	very deep red
2	2.3	very deep red
3	4.9	medium red
4	5.4	quite pale
8	3.5	almost colorless

Evidences of chemical change with dilution are sharp change of color, and maxima and minima on the conductivity curves. Further study reveals that ether in the ethyl bromide combines quantitatively with the aluminum chloride mole for mole, and that the sharp changes in color and conductivity observed upon adding portions of aluminum chloride to ethyl bromide-aromatic hydrocarbon mixtures were entirely due to this impurity. With carefully purified materials neither maxima or minima nor color changes were observed, as seen in the following table:

Naphthalene (0.8074 g in 5 cc of ethyl bromide)

$AlCl_3$ (g)	Resistance (ohms)	Color	V	μ (mhos)
0 0220	2730	deep red	30 34	4 44
.0420	1128	deep red	15.90	5.64
.0870	390	deep red	7 67	7.84
1795	161	deep red	3 72	9.23
.3335	80	deep red	2.00	10 20
.4050	60	deep red	1.65	10 86
.4880	50	deep red	1 37	10.88
.5445	47	deep red	1.226	10.40

By the addition of aluminum chloride, representatives of two classes of substances, namely, the alkyl halides and the aromatic hydrocarbons, which have been regarded as media incapable of sharing directly in the production of ions, have been shown to become good conductors. The conductivity has been traced to the formation of compounds by virtue of the potential valence of certain atoms which they contain. The formation of these compounds and their comparative stability in the Friedel-

Crafts reaction is evidenced by the fact that very little acid is evolved until the concentration of aluminum chloride passes a certain value. In some instances, therefore, the proof seems conclusive that chemical reaction is the cause and ionization the effect of subjecting the substances selected to those reactions to which experience has shown them to be peculiarly liable. If the aromatic hydrocarbon is used as solvent for aluminum chloride and ethyl bromide, no trace of conductivity is observed until sufficient additions have been made to have a lower layer separate out. Then conductivity is observed only in the lower layer. Walker and Spencer [93] found the conductivity of aluminum chloride in ether solution at 18° to be:

v	μ
3.58	0.09

Wertyporoch and Firla [94] measured the conductivity of aluminum chloride in several chlorinated hydrocarbons. The molar conductivity in ethyl chloride scarcely varies with the concentration. The specific conductivity of a 3.5% solution = 4.400×10^{-5} and the molar conductivity between 0.025 and 0.2 mole/liter remains constant at 0.2 mho. The specific conductivity of the solvent is less than 3×10^{-9}. The solvates of Al_2Cl_6 and Al_4Cl_{12} are $[Al(C_2H_5Cl)_n]AlCl_6$ and $[Al(C_2H_5Cl)_m](AlCl_4)_3$ respectively; they are completely ionized to give ions which are stable upon dilution. The ionization equations are:

$$[Al(C_2H_5Cl)_n]AlCl_6 = [Al(C_2H_5Cl)_n]^{+++} + {}^{---}AlCl_6$$
$$[Al(C_2H_5Cl)_m](AlCl_4)_3 = [Al(C_2H_5Cl)_m]^{+++} + {}^{---}(AlCl_4)_3$$

Solutions of aluminum chloride in *n*-propyl chloride, isopropyl chloride, and chlorocyclohexane show much greater conductivity than in ethyl chloride. A 2.8% solution in normal propyl chloride has a specific conductivity of 1.476×10^{-3}. A 2.6% solution in isopropyl chloride has a specific conductivity of 1.384×10^{-3}. In preparing the solutions an evolution of hydrogen chloride is evident, and the solutions become yellow changing to red-brown, with formation of unsaturated hydrocarbons. These unsaturated hydrocarbons are incorporated in a complex with aluminum chloride. Conductivity measurements give values about thirty times higher in these than in ethyl chloride solutions, which indicates a strongly bonded complex. Results secured by these investigators are listed in the tables on page 34.

Salt-like compounds are formed when aluminum chloride is dissolved in benzoyl chloride and in acetyl chloride. These compounds become part of the cation.

The addition of benzene to all these solutions increases the conductivity, but the addition of cyclohexane to aluminum chloride in chlorocyclohexane does not change the conductivity; in the case of ethyl chloride the increase is 108 times, and with the others about 1.5 times. In all

[93] J. W. Walker and A. Spencer, *J. Chem. Soc.*, 85, 1106-1110 (1904)
[94] E. Wertyporoch and T. Firla, *Z. physik. Chem.*, 162, 398-414 (1932); *Brit. Chem. Abstracts-A*, 127 (1933).

Chlorocyclohexane + $AlCl_3$

C^* (Mol-liter)	V^* (liters)	$L \cdot 10^7$ *	μ^*
0.0042	236.0	13.5	0.32
0.0104	95.8	41.6	0.39
0.0184	54.4	89.9	0.49
0.0496	20.2	369.2	0.74
0.0725	13.8	579.6	0.80
0.0970	10.3	835.0	0.86
0.1206	8.29	1130	0.94
0.2014	4.96	1790	0.89

Ethyl Chloride + $AlCl_3$

C (Mol-liter)	V (liters)	$L \cdot 10^7$	μ
0.0293	34.2	74.3	0.25
0.0398	25.1	95.8	0.24
0.0476	21.0	111.5	0.25
0.0648	15.4	138.3	0.21
0.0760	13.1	158.6	0.20
0.0960	10.4	183.0	0.19
0.1146	8.72	212.5	0.18
0.1868	5.35	334.0	0.18
0.2360	4.23	440.0	0.18

Propyl Chloride + $AlCl_3$

0.0045	224.2	22.5	0.50
0.0130	76.7	55.1	0.42
0.0200	49.9	110.0	0.55
0.0468	21.4	1005	2.15
0.0806	12.4	3179	3.98
0.1500	6.68	6200	4.14
0.2136	4.68	14761	6.91
0.2374	4.21	15233	6.42

Isopropyl Chloride + $AlCl_3$

0.0039	259	65.7	1.60
0.0116	86.4	254.0	2.20
0.0197	50.7	518.0	2.62
0.0333	30.0	628.0	1.89
0.0566	17.7	1417	2.50
0.0728	13.7	2452	3.40
0.0868	11.5	3648	4.20
0.1130	8.85	5960	5.30
0.1348	7.41	7700	5.80
0.1546	6.47	9600	6.22
0.1976	5.06	13840	7.01

* In these tables C is the concentration in moles per liter, V is dilution in liters per mole, L is the specific conductivity, and μ is the molar conductivity.

cases hydrogen chloride is produced upon the addition of benzene, but this is without influence on the conductivity. The maximum conductivity is not reached until after twelve to twenty-four hours. Wertyporoch and Firla portray graphically the influence of addition of benzene to ethyl, propyl, and isopropyl chloride; their tabulated data follow:

50 cc. solvent, 0°C

Alkyl Chloride	$AlCl_3$ (g.)	Benzene (cc.)	L (at start)	L (at end)	$\frac{L \text{ (at end)}}{L \text{ (at start)}}$
Ethyl chloride	1.5741	1	4.400×10^{-5}	4.755×10^{-3}	108
Propyl chloride	1.5814	1	1.523×10^{-3}	2.043×10^{-3}	1.4
	1.5563	1	1.520×10^{-3}	2.414×10^{-3}	1.6
Isopropyl chloride	1.3128	1	1.384×10^{-3}	1.772×10^{-3}	1.3
	1.2763	1	1.225×10^{-3}	1.979×10^{-3}	1.6

The authors explain the increase in conductivity by assuming primary formation of a pseudo-salt of aluminum chloride with the organic halide, which later changes to the normal salt complex of the aluminum chloride with the resulting unsaturated hydrocarbon. The aromatic hydrocarbon is in the cation with the aluminum.

The table (p. 35, top) shows the effect on conductivity of adding benzene derivatives to the alkyl chloride solutions of aluminum chloride.

Pure acetyl chloride and benzoyl chloride have low specific conductivities; *i.e.*, $L = 3.20 \times 10^{-7}$ and 2.99×10^{-7} at 0°C. The addition of aluminum chloride lowers the molar conductivity of these solvents. When

Alkyl Chloride	$AlCl_3$ (g)	-benzene (g)	L (at start)	L (at end)	$\frac{L \text{ (at end)}}{L \text{ (at start)}}$
Ethyl chloride	1.5799	hexaethyl- 2.7909	5.310×10^{-5}	5.388×10^{-5}	102
Isopropyl chloride	1.33	isopropyl- 0.0864	1.304×10^{-4}	1.480×10^{-3}	1.1
	1.33	isopropyl- 1.7280	1.304×10^{-4}	1.336×10^{-3}	1.03
	0.8132	tri-isopropyl- 1.2309	5.250×10^{-4}	7.245×10^{-4}	1.41
Propyl chloride	0.7154	dipropyl- 1.8440	5.115×10^{-4}	7.495×10^{-4}	1.47

benzene is added to these solutions the conductivity rises, hydrogen chloride is evolved, and the solutions take on dark colors.

These effects are shown in the following tables:

Benzoyl Chloride + $AlCl_3$

C (Mol-liter)	V (liters)	$L \cdot 10^7$	μ
0.0038	260.0	299.5	8.0
0.0086	115.7	614.0	7.0
0.0182	54.9	683.0	3.7
0.0379	26.4	813.0	2.1
0.0612	16.3	966.0	1.6
0.0988	10.1	1151	1.2
0.1282	7.80	1412	1.1
0.1676	5.97	1532	0.9
0.2026	4.94	2015	1.0
0.2830	3.53	2533	0.9
0.3992	2.50	3415	0.9
0.6260	1.59	4835	0.8
0.6910	1.44	5224	0.8

Acetyl Chloride + $AlCl_3$

C (Mol-liter)	V (liters)	$L \cdot 10^7$	μ
0.0024	422.0	509.0	21.5
0.0064	156.7	1018	15.8
0.0107	93.2	1423	13.3
0.0220	45.5	2150	9.8
0.0438	22.8	2470	5.6
0.1263	7.91	9310	7.3
0.1751	5.71	12790	7.3
0.1982	5.04	16170	8.1
0.2412	4.14	13150	5.6
0.3204	3.12	22880	7.1
0.3916	2.55	26520	6.7
0.4370	2.29	33280	7.5
0.5240	1.90	39180	7.4
0.6260	1.59	49790	7.9

Addition to Acetyl and Benzoyl Chloride

(50 cc. solvent)

Acid Chloride	$AlCl_3$ (g)	Benzene (cc)	L (at start)	L (after 22 hrs)	$\frac{L \text{ (at end)}}{L \text{ (at start)}}$
Acetyl chloride 0°C	1.38	1	1.639×10^{-3}	2.385×10^{-3}	1.5
Benzoyl chloride 18°C	5.1907	5	5.224×10^{-4}	8.500×10^{-4}	1.6
	5.1888	4	5.220×10^{-4}	1.111×10^{-3}	2.1

If instead of benzene there is added acetophenone and benzophenone, respectively, similar results are obtained, as is shown in the following table:

Acetyl Chloride and Acetophenone, Benzoyl Chloride and Benzophenone

(50 cc. solvent)

Acid Chloride	$AlCl_3$ (g)	Ketone (g)	L (at start)	L (at end)	$\frac{L \text{ (at end)}}{L \text{ (at start)}}$
Acetyl chloride	1.3200	acetophenone 1.1950	1.650×10^{-4}	1.769×10^{-4}	1.1
Benzoyl chloride	5.1448	benzophenone 7.8295	4.000×10^{-4}	5.208×10^{-4} (constant)	1.3
		after 10 hrs.		7.550×10^{-4}	1.9

By the addition of pentane as well as cyclohexane to aluminum chloride solutions in acetyl chloride there is no conductivity increase. There is formation of a heavy oil which settles out.

By electrolysis of their solutions, and subsequent decomposition and analysis of the materials concentrated at each electrode, these authors have studied the ratios of the organic materials associated with aluminum chloride.

Compounds of Aluminum Chloride with Inorganic Substances

Ammonia

As long ago as 1830 the compound of aluminum chloride with ammonia was prepared and reported by Persoz [95] to be $Al_2Cl_6,6NH_3$. In 1832 Rose [96] obtained a similar product.

Subsequently it was concluded that two complexes existed, namely, $Al_2Cl_6,6NH_3$ and $Al_2Cl_6,2NH_3$. Later another compound, $Al_2Cl_6,12NH_3$, was announced. This was a bulky, white solid, with a high ammonia vapor pressure. Upon heating it in dry hydrogen, $AlCl_3,2NH_3$, a hygroscopic solid, was formed. Water decomposed this, yielding aluminum hydroxide.[97]

The heat of formation of $AlCl_3,2NH_3$, its low hygroscopicity, and its slow decomposition in moist air indicate that it is a very stable compound.[98]

$Al_2Cl_6,10NH_3$ melts at 380° and boils at 450° with $Al_2Cl_6,2NH_3$ as the distillate when distilled with hydrogen, and $Al_2Cl_6,4.61NH_3$ when distilled without hydrogen.[99] This is considered to be a mixture of $Al_2Cl_6,2NH_3$ and $Al_2Cl_6,10NH_3$. At liquid ammonia temperature, $Al_2Cl_6,10NH_3$ absorbs NH_3 to form $Al_2Cl_6,18NH_3$.

There is some question as to whether these compounds are formulated correctly, since the actual data show 2.33, 6.33, 10.33, 12.33, and 18.33 NH_3 molecules for each Al_2Cl_6. This would indicate single molecules of the formula $3Al_2Cl_6,3nNH_3$, whereas Deville and Troost [100] found smaller molecules in the vapor phase at 350°.

The stability of these compounds is comparable with that of the hydrates. The heats of formation of these associated molecules have been determined by Baud [101] as follows:

$Al_2Cl_6 + 2.33NH_3$	+ 77.6 Cal.
$Al_2Cl_6 + 6NH_3$	+ 167.54 Cal.
$Al_2Cl_6 + 10NH_3$	+ 245.23 Cal.
$Al_2Cl_6 + 12NH_3$	+ 268.23 Cal.
$Al_2Cl_6 + 18NH_3$	+ 317.85 Cal.

[95] J. F. Persoz, *Ann. chim. phys (2)*, 44, 319 (1830).
[96] H. Rose, *Pogg. Ann.*, 24, 298 (1832)
[97] J. M. Stillman and B. Yoder, *Am. Chem. J.*, 17, 748-753 (1895); *J. Chem. Soc. Abs*, 70, (II), 301 (1896).
[98] E. Baud, *Ann. chim. phys. (8)*, 1, 8-72 (1904).
[99] E. Baud, *Compt. rend.*, 132, 134-136 (1901); *J. Chem. Soc. Abs*, 80 (II), 161 (1901).
[100] H. St. C. Deville and L. J. Troost, *Ann. chim. phys.*, 58 (3), 257 (1860).
[101] E. Baud, *Ann. chim. phys. (8)*, 1, 8-72 (1904); *J. Chem. Soc. Abs.*, 86 (II), 176 (1904).

The difference of 49.62 Calories between the last two compounds for the addition of $6NH_3$ gives 8.27 Calories per molecule of NH_3, which is employed in the Clapeyron formula to calculate the dissociation pressures.

The variation in entropy is 32.004 as determined from this expression or from the curve of dissociation pressure.[102]

The heats of solution of these ammonia complexes are [103]:

$Al_2Cl_6,18NH_3$	15.88 Cal. in 44 l. H_2O at 15°
$Al_2Cl_6,12NH_3$	12.70 Cal. in 48 l. H_2O at 15°
$Al_2Cl_6,10NH_3$	18.10 Cal. in 44 l. H_2O at 15°
$Al_2Cl_6,6NH_3$	60.59 Cal. in 44 l. H_2O at 15°
$Al_2Cl_6,2.33NH_3$	106.09 Cal. in 44 l. H_2O at 15°

$Al_2Cl_6,2.33NH_3$ dissolves in water as a clear solution. The others give first a precipitate of hydroxide which gradually dissolves to a clear solution.[104]

Hydrogen chloride gas acts on all the Al_2Cl_6,nNH_3 complexes to form $Al_2Cl_6,2.33NH_3 + NH_4Cl$. This indicates the $Al_2Cl_6,2.33NH_3$ to be a very stable complex. If, however, it is distilled in a current of hydrogen chloride gas all the ammonia is removed to form ammonium chloride.[105]

An extensive study of ammonio-complexes of aluminum chloride is presented by Clark [106] who gives a description of the apparatus for composition-temperature determinations. He tabulates composition-temperature-pressure data and heats of dissociation and discusses the relationships between the fundamental property of stability and other properties.

Klemm and Tanke [107] studied the constitution of aluminum halide ammoniates. The density increases from chloride to iodide. The density decreases from AlX_3,NH_3 to $AlX_3,6NH_3$. The molecular volume increases from chloride to iodide. The molecular volume decreases from AlX_3,NH_3 to $AlX_3,6NH_3$; but the cation becomes larger, the salt changing to the ionic lattice. The mono-ammine is an additive salt, whereas the tri-, pent-, and hexammines are complex salts having the NH_3 groups attached to the cation. The heats of formation increase from the chloride to the iodide. The behavior and properties correspond to the chromium and indium salts.

Reduction of aluminum chloride mono-ammine to aluminum nitride results from treating the fused ammine with metallic aluminum. A complex compound, $AlCl_3.AlN$, stable at near red heat, is formed with evolution of hydrogen.[108]

[102] E. Baud, *Compt. rend.*, 132, 690-692 (1901); *J. Chem. Soc. Abs.*, 80 (II), 303 (1901).
[103] W. A. Roth and A. Buchner, *Z. Elektrochem.*, 40, 87-89 (1934); *C. A.*, 28, 2257.
[104] E. Baud, *Ann. chim. phys. (8)*, 1, 8-72 (1904); *J. Chem. Soc. Abs.*, 86 (II), 176 (1904).
[105] E. Baud, *loc. cit.*; *Compt. rend.*, 132, 553-556 (1901); *J. Chem. Soc. Abs.*, 80 (II), 224 (1901).
F. Ephraim and S. Millman, *Ber.*, 50, 529-541 (1917); *C. A.*, 11, 2979; *J. Chem. Soc. Abs.*, 112 (II), 319-320 (1917).
[106] G. L. Clark, *Am. J. Sci.*, 7, 1-23 (1924); *C. A.*, 18, 921
[107] W. Klemm and E. Tanke, *Z. anorg. allgem. Chem.*, 200, 343-366 (1931).
[108] V. A. Plotnikov and P. T. Kalita, *J. Gen. Chem. (U.S.S.R.)*, 3, 872-873 (1933); *C. A.*, 28, 3019 (1934). W. Biltz, *Z. anorg. Chem.*, 89, 141-163 (1914); *J. Chem. Soc. Abs.*, 108 (II), 440 (1915).

Sulfur Dioxide

$AlCl_2,SO_2Cl$ is formed by the reaction of aluminum chloride on sulfur dioxide, rapidly at 50-60°, and slowly at room temperature.[109] One mole of the aluminum halide apparently combines with one mole of sulfur dioxide at low temperatures.[110]

$Al_2Cl_6,2SO_2$ was prepared by Adrianowsky [111] in 1879. From this he was able to prepare $AlCl_2,SO_2,C_6H_5$; $Al(OH)_2,SO_2,C_6H_5$; and C_6H_5,SO_2H. Baud [112] found a positive heat of reaction when sulfur dioxide was passed into aluminum chloride, forming a pasty mass of the composition Al_2Cl_6, SO_2. With further addition of sulfur dioxide, requiring a long period, the product becomes a clear, colorless, limpid liquid of the composition $Al_2Cl_6,2SO_2$. With liquid sulfur dioxide the reaction is more rapid. By subliming aluminum chloride in a current of sulfur dioxide a product is obtained which is a yellow-orange solid at 4°, decomposes at 80°, and distills at 200°, yielding a distillate of the composition Al_2Cl_6,SO_2. Sulfur tetrachloride was detected in the distillate. By the direct action of liquid sulfur dioxide on aluminum chloride in a sealed tube Ruff [113] obtained a well-defined crystalline compound, $AlCl_3,SO_2$. It is stable at 100° in an atmosphere of sulfur dioxide. In sulfuryl chloride solution, it can be entirely decomposed at room temperature by carrying off the free sulfur dioxide with a current of dry carbon dioxide. The compound, therefore, is quite unstable, having a high sulfur dioxide vapor pressure at ordinary temperatures.

Sulfur Chlorides

Aluminum chloride reacts with sulfur monochloride with or without the addition of sulfur, yielding a series of compounds, one of which is a complex compound of sulfur dichloride. $AlCl_3,2S_2Cl_2$ is another product; upon heating it yields S_2Cl_2, Cl_2, and $AlCl_3,SCl_2$. The $AlCl_3,SCl_2$ upon further heating yields $AlCl_3,SCl_4$ and SCl_2. The product $AlCl_3,SCl_4$ is the most stable product and may be crystallized. Upon addition of sulfur to the mixture of $AlCl_3,SCl_4$ and SCl_2, $AlCl_3,SCl_2$ is regenerated.

When heating different proportions of $AlCl_3,S_2Cl_2$ and sulfur in sealed tubes $AlCl_3,2S_3Cl_2$ and $AlCl_3,2S_4Cl_2$ are obtained. $AlCl_3,2S_2Cl_2$ and $AlCl_3,SCl_2$ dissociate only slightly at room temperature, whereas $AlCl_3,2S_4Cl_2$ dissociates appreciably. If $AlCl_3,2S_4Cl_2$ is extracted with carbon disulfide, a residue of $AlCl_3,2S_2$ remains, and further extraction leaves $AlCl_3,S_2$. Extraction of $AlCl_3,2S_2Cl_2$ with carbon disulfide leaves a residue of $AlCl_3,S_2$. These compounds decompose when distilled.

Treating S_2Cl_2 with metallic aluminum produces $AlCl_3,3S_3Cl_2$. The latter yields $AlCl_3,S_2$ upon extraction with carbon disulfide. Heating S_2Cl_2 with metallic aluminum yields $AlCl_3,3S$.

[109] G. Wagner, *Ber.*, 12, 686-689 (1879). G. Gustavson, *Bull. soc. chim. (2)*, 42, 325-327 (1884); *J. Chem. Soc. Abs.*, 48, 383 (1885).
[110] F. Ephraim and I. Kornblum, *Ber.*, 49, 2007-2021 (1916); *J. Chem. Soc. Abs.*, 110 (II), 614-615 (1916); *C. A.*, 11, 1066.
[111] M. Adrianowsky, *Bull. soc. chim. (2)*, 31, 495 (1879).
[112] E. Baud, *Ann. chim. phys. (8)*, 1, 62-72 (1904); *J. Chem. Soc. Abs.*, 86 (II), 176 (1904).
[113] O. Ruff, *Ber.*, 35, 4453-4470 (1902); *J. Chem. Soc. Abs.*, 84 (II), 149 (1903).

$AlCl_3,3S_3Cl_2$ is coördinated, since upon distillation all the aluminum chloride appears in the distillate with no residue of aluminum sulfide.

The compounds as obtained in this work were not pure. Owing to their instability, to their slow solubility in S_2Cl_2, and to their readiness to change from one to another, they were produced in only the liquid state.[114]

Hydrogen Sulfide

Wöhler [115] found that by distilling aluminum chloride in a current of hydrogen sulfide some of the hydrogen sulfide became fixed.

In the presence of moist air the aluminum chloride-hydrogen sulfide complex loses hydrogen sulfide. By heating aluminum chloride in a current of hydrogen sulfide, Baud [116] obtained pearly plates composed of $Al_2Cl_6,0.1H_2S$ up to $Al_2Cl_6,0.3H_2S$. If aluminum chloride is treated with liquid hydrogen sulfide at $-70°$, $Al_2Cl_6,2H_2S$ is obtained. This is stable below $-45°$. At room temperature it evolves one mole of hydrogen sulfide, leaving Al_2Cl_6,H_2S which is stable at room temperature, its dissociation pressure being 760 mm at 60°. It is decomposed with water, the heat of dissolution being +150.56 Calories per mole. The heat of formation is +9.45 Calories, for the reaction

$$Al_2Cl_6 + H_2S \text{ (gas)} \longrightarrow Al_2Cl_6,H_2S$$

Calculated from Trouton's rule, it is 9.99 Calories. Biltz [117] obtained 9.22 Calories at 0°.

Al_2Cl_6,H_2S decomposes at +14°, the pressure of hydrogen sulfide being 100 mm. The density of $AlCl_3,H_2S$ is 2.162 at $-30°$. The molar volume is 23 to 24 cc.

Hydrogen Cyanide

Karantassis [118] prepared $AlCl_3,2HCN$ by adding hydrogen cyanide to aluminum chloride in a U-tube cooled in an ice and salt mixture. The excess hydrogen cyanide was then driven off by allowing the mixture to warm up to 30°. The product liquefies at 100° with loss in weight.

The ability of aluminum chloride to attach hydrogen cyanide has been utilized in preparing fumigating materials.[119]

The addition of hydrogen cyanide to aluminum chloride at room temperature was reported by Hinkel and Dunn [120] to cause a vigorous reaction. First a liquid is formed, and from this $AlCl_3,2HCN$ precipitates. If the aluminum chloride is suspended in benzene, addition of hydrogen cyanide occurs when the latter is added to the suspension. The addition compound has an appreciable vapor pressure since hydrogen cyanide is

[114] O. Ruff and H. Golla, *Z. anorg. allgem. Chem.*, 138, 17-32 (1924); *C. A.*, 19, 221.
[115] F. Wöhler, *Ann. chim. phys. (3)*, 37, 60 (1828).
[116] E. Baud, *Compt. rend.*, 134, 1429-1431 (1902); *J. Chem. Soc. Abs.*, 82 (II), 505 (1902).
[117] W. Biltz and E. Keunecke, *Z. anorg. allgem. Chem.*, 147, 171-187 (1925); *C. A.*, 19, 3226.
[118] T. Karantassis, *Compt. rend.*, 194, 461 (1932); *C. A.*, 26, 2365.
[119] U. S. P. 1,750,196 (1930) to H. Lehrecke (to Roessler and Hasslacher Chem. Co.); *Brit. Chem Abstracts-B*, 558 (1931).
[120] L. E. Hinkel and R. T. Dunn, *J. Chem. Soc.*, 3343 (1931); *C. A.*, 26, 1208.

evolved from the material in a vacuum desiccator. At 100° all the hydrogen cyanide is evolved. The compound is unstable in moist air and also in ether solution.

Oxides of Nitrogen

Besson [121] first studied the action of the oxides of nitrogen on metallic chlorides, finding that combination occurs with several of these, including aluminum chloride. He found the compound of aluminum chloride with nitric oxide to be more stable than that with nitrogen tetroxide. Both are decomposed by water.

These results were verified by Thomas.[122] The combination of nitric oxide with aluminum chloride is a slow process, yielding an extremely hygroscopic, pale-yellow compound, Al_2Cl_6NO, which melts without decomposition in a sealed tube.

Nitrosyl Chloride

The compound $AlCl_3.NOCl$ may be prepared by treating powdered aluminum chloride or a solution of the salt in carbon tetrachloride with liquid nitrosyl chloride.[123]

Phosphorus Compounds

When freshly precipitated clay is heated in phosphorus pentachloride vapor a compound $AlCl_3.PCl_5$ results. It may also be prepared by heating metallic aluminum with phosphorus pentachloride.[124]

The melting point curve for the system $AlCl_3,PCl_5$ has been determined, and the existence and stability of the compound $AlPCl_8$ confirmed. Vapor density measurements show that in the vapor it is largely dissociated. Its low volatility indicates an ionic structure. Its melting point was found to be 380°.[125]

A combination of aluminum chloride with phosphoryl chloride results when a mixture of them is heated in a closed tube. Moisture decomposes this into aluminum hydroxide, hydrogen chloride, and orthophosphoric acid.[126]

$Al_2Cl_6,1/3PH_3$ has been prepared by Rose.[127] Other investigators [128] have not been able to confirm formation of this compound. Later Höltje and Meyer [129] found that if 0.6 mole of phosphine is reacted for a short time with 1 mole of aluminum chloride at 70°, the compound $AlCl_3,PH_3$ is readily formed.

[121] A. Besson, *Compt. rend.*, 108, 1012 (1889); *J. Chem. Soc. Abs.*, 56, 934 (1889).
[122] V. Thomas, *Compt. rend.*, 121, 128-130 (1895); *J. Chem. Soc. Abs.*, 68 (II), 495 (1895).
[123] H. Rheinboldt and R. Wasserfuhr, *Ber.*, 60, 732-737 (1927). H. Gall and H. Mengdehl, *Ber.*, 60, 88-91 (1927).
[124] E. Baudrimont, *Compt. rend.*, 55, 863 (1863); *Ann. chim. phys. (4)*, 2, 41 (1864).
[125] W. Fischer and O. Jübermann, *Z. anorg. Chem.*, 235, 337-351 (1938); *Brit. Chem. Abstracts-A* (I), 240 (1938).
[126] W. Casselmann, *Ann.*, 98, 220 (1856).
[127] H. Rose, *Pogg. Ann.*, 24, 295 (1832).
[128] W. Peters, *Z. anorg. Chem.*, 89, 208 (1914). R. Höltje, *Z. anorg. Chem.*, 190, 253 (1930).
[129] R. Höltje and F. Meyer, *Z. anorg. Chem.*, 197, 93-102 (1931).

Phosgene

Liquid phosgene dissolves aluminum chloride. The heat of solution has not been determined, but the thermal effect is not great. Upon evaporation of such a solution at room temperature, there remains a colorless liquid having a freezing point of $-2°$, the composition $2AlCl_3,5COCl_2$, and a dissociation tension of 760 mm at 30°. Upon subsequent heating, this product is converted into $2AlCl_3,3COCl_2$ which has a dissociation tension of 760 mm at 55°. Upon further removal of phosgene, a silky needle-like residue, $4AlCl_3,COCl_2$, stable at 750°, remains. These last two compounds may be prepared by distilling aluminum chloride in a current of dry phosgene, or by leading the vapor of aluminum chloride by means of a current of carbon dioxide through a red-hot tube. Commercial aluminum chloride containing these two compounds may be purified by fractional sublimation in a current of hydrogen or nitrogen.[129a] The great chemical activity of aluminum chloride as displayed in a variety of ways in both organic and inorganic chemistry suggested that the solution in phosgene might have unusual properties. Metallic potassium, which does not react with phosgene, does react with a phosgene-aluminum chloride solution. The metal becomes slowly corroded and gas is evolved. The product is a phosgenate of a slightly soluble double salt of potassium chloride and aluminum chloride.[130]

Germann[131] considers the system aluminum chloride dissolved in phosgene as an acid system, comparing $2AlCl_3,COCl_2$ to $2SO_3,H_2O$. Metals replace the CO giving salts, $2AlCl_3,MCl_2$.

$$COAl_2Cl_6 + Ca \longrightarrow CaAl_2Cl_6 + CO$$

With metallic chlorides the system gives phosgeno- salts:

$$\underset{\text{acid}}{COAl_2Cl_6} + \underset{\text{base}}{CaCl_2} \longrightarrow CaAl_2Cl_8 + COCl_2$$

The CO acts as hydrogen in an acid.[132] The phosgenate produced in the foregoing example has been found by vapor pressure measurements to be $CaAl_2Cl_8,2COCl_2$.[132]

The following phosgeno-aluminates have also been prepared[133]:

Compound by analysis
$NaAlCl_4$
$CaAl_2Cl_8$
$SrAl_2Cl_8$
$BaAl_2Cl_8$

The preparation of the metallic chloroaluminates in sealed Faraday tubes is by the action of the metal on phosgene in the presence of aluminum chloride. The reactions are rapid, with evolution of heat and

[129a] E. Baud, *Compt. rend.*, 140, 1688-89 (1905), *J. Chem. Soc. Abs.*, 88 (II), 525 (1905).
[130] A. F. O. Germann, *J. Phys. Chem.*, 28, 879-887 (1924); *C. A.*, 18, 3330.
[131] A. F. O. Germann, *Science*, 61, 71 (1925); *C. A.*, 19, 765.
[132] A. F. O. Germann and C. R. Timpany, *J. Am. Chem. Soc.*, 47, 2275-2278 (1925).
[133] A. F. O. Germann and D. M. Birosel, *J. Phys. Chem.*, 29, 1469-1476 (1925); *C. A.*, 20, 534.

carbon monoxide. The order of metals with respect to their rates of reaction is Ca = Mg > K > Cd > Zn > Sn. The slow rate for the last three metals is in part due to incrustation formations.[134]

Metallic Chlorides

Baud [135] prepared several double halides of aluminum chloride. The method used consisted in heating in a sealed tube at 250-300° a mixture of the two halides in the ratio desired for compound formation. Fusion occurs in this temperature range for Al_2Cl_6 + 2NaCl. If 3NaCl is used, the temperature must be raised to 500°. With excess aluminum chloride, the excess over the equivalent necessary for compound formation distills to the cool portion of the tube, indicating that the homogeneous product is probably a compound and not a true solution.

The following data are given for the double salts prepared:

Salt	Molar heat of solution in 32 liters H_2O
Al_2Cl_6,2NaCl	141 42 Cal. at 15°
Al_2Cl_6,2KCl	120.44
Al_2Cl_6,2NH_4Cl	120.943
Al_2Cl_6,3NaCl	136.97
(prepared at 500° by Al_2Cl_6,2NaCl + NaCl)	
Al_2Cl_6,3KCl	112.07
Al_2Cl_6,6NaCl	129.73 (48 liters H_2O)
Al_2Cl_6,6KCl	93.304 (48 liters H_2O)
Al_2Cl_6,2AgCl	151.45 (at 22°)
Al_2Cl_6,1.5$CaCl_2$	173.40 (at 16°)
Al_2Cl_6,1.5$SrCl_2$	164.39 (at 16°)
Al_2Cl_6,$BaCl_2$	153.52 (at 22° in 8 liters H_2O)
(prepared at 300°)	
Al_2Cl_6,1.5$BaCl_2$	
(prepared by heating Al_2Cl_6,$BaCl_2$ to 500°)	
Al_2Cl_6,1.5$ZnCl_2$	187.99

Heat of fixation of each mole of metallic chloride:

	NaCl	KCl	AgCl	$CaCl_2$	$SrCl_2$	$BaCl_2$	NH_4Cl
Each of the first two moles	5.90	13.19	2.51	6.18	5.81	5.29	13.26
The third	3.45	4.15					
Each of the fourth to sixth	1.41	2.035					
The seventh	0.39	0.75					

These salts possess a fibrous structure; they distill without decomposition in a current of hydrogen or nitrogen. Al_2Cl_6,$SrCl_2$ and Al_2Cl_6,$CaCl_2$ could not be prepared since they dissociate below 300°. Al_2Cl_6,1.5$ZnCl_2$ is a pasty, translucent mass when first prepared, remaining in a suspended state for some time. It loses Al_2Cl_6 at 400° showing it to be less stable than the other double salts.

Ammonia gas was found to combine readily with these double salts at ordinary temperature, forming Al_2Cl_6,2MCl,12NH_3. The heat evolved in the general reaction Al_2Cl_6,2MCl + 12NH_3 = Al_2Cl_6,2MCl,12NH_3 is 252-255 Calories per mole, or 21 Calories per mole of fixed ammonia.

[134] A. F. O. Germann and K. Gagoe, *J. Phys. Chem.*, **28**, 965-972 (1924); *C. A.*, **18**, 3330.
[135] E. Baud, *Compt. rend.*, **133**, 869-871 (1901); *J. Chem. Soc. Abs.*, **82** (II), 142 (1902); *Ann. chim. phys. (8)*, **1**, 8-72 (1904); *J. Chem. Soc. Abs.*, **86** (II), 176 (1904).

The heats of solution of the ammoniated double salts are:

$Al_2Cl_6,2NaCl,12NH_3$	+ 11.23 Cal.
$Al_2Cl_6,2NH_4Cl,12NH_3$	− 5.47 Cal.
$Al_2Cl_6,2KCl,12NH_3$	− 6.08 Cal.

In their study of the factors influencing compound formation and solubility in fused salt mixtures, Kendall and co-workers [136] have given us a great deal of information on the solubility of aluminum chloride in several inorganic salts, together with the kinds of double salts formed. They used great care in preparing the anhydrous salts. Their method consisted in adding the metallic chloride to aluminum chloride and noting the temperature at which the solid phase disappeared. From the temperature-per cent composition curves they determined the composition of the double salts formed. Their data follow:

Systems Containing Aluminum Chloride as Reference Salt

(The given temp. indicates disappearance of the solid phase)

Lithium Chloride

% LiCl	6.6	17.2	20.1	29.6	38.4	40.1	43.2	45.8	47.4
Temp. (°C)	190.0	187.9	186.4	171.4	125.6	114.4	117.8	132.8	139.9
Solid phase			$AlCl_3$					$AlCl_3$,LiCl	

49.6	49.6	50.5	
143.0	170.4	338.5	
	LiCl		

Sodium Chloride

% NaCl	20.1	22.1	26.1	30.6	33.9	37.3	41.1	44.8	47.6
Temp. (°C)	192.0[a]	190.0	182.0	169.4	151.3	130.2	123.6	140.7	147.9
Solid phase	xAlCl$_3$,yNaCl							AlCl$_3$,NaCl	

48.3	48.4	49.5	
151.9	153.7	320.5	
		NaCl	

[a] A two liquid layer region extends from below 0.2 to 18.0% of sodium chloride, in equilibrium with solid phase xAlCl$_3$,yNaCl at 193.5°. Coalescence temperatures lie too high for determination.

Potassium Chloride

% KCl	19.0	23.0	27.0	31.2	34.5	37.5	42.9	48.8	49.5
Temp. (°C)	192.5[a]	187.4	177.2	162.1	158.4	178.7	213.1	248.4	255.5
Solid phase	xAlCl$_3$,yKCl					AlCl$_3$,KCl			

51.5	
375.0	
KCl	

[a] A two liquid layer region extends from below 0.4 to 18.2% of potassium chloride, in equilibrium with solid phase xAlCl$_3$,yKCl, at 193.0°.

Ammonium Chloride

% NH_4Cl	0.2	20.6	23.8	28.5	31.9	33.2	36.9	38.2	43.5
Temp. (°C)	192.2	192.3[a]	186.6	171.8	157.9	173.4	229.4	239.7	274.1
Solid phase	xAlCl$_3$,yNH$_4$Cl					AlCl$_3$,NH$_4$Cl			

49.1	53.1	56.8	58.4	61.0	65.1	
301.2	287.2	266.1	257.1	284.3	357.0	
AlCl$_3$,NH$_4$Cl				NH$_4$Cl		

[a] A two liquid layer region extends from 0.2 to 20.5% of ammonium chloride, in equilibrium with solid phase xAlCl$_3$,yNH$_4$Cl at 192.5°.

[136] J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Am. Chem. Soc.*, 45, 963-996 (1923); *C. A.*, 17, 1914.

Cuprous Chloride

% CuCl	10.5	19.7	29.0	30.8	32.2	40.6	47.9	48.1	50.9
Temp. (°C)	190.0	187.4	178.4	175.3	178.3	209.9	230.9	231.6	231.9
Solid phase			$AlCl_3$				$AlCl_3$,CuCl		
	54.0	57.4	60.1	62.0					
	225.9	227.4	252.5	291.5					
			CuCl						

Silver Chloride

% AgCl	0.38	20.1	26.5	32.0	33.4	38.0	39.7	39.9	43.6
Temp. (°C)	191.2[a]	190.1	184.5	161.5	156.0	136.8	121.9	122.2	138.9
Solid phase			xAlCl$_3$,yAgCl					$AlCl_3$,AgCl	
	47.0	47.9	49.1	50.8					
	147.5	175.4	285.3	378.0					
			AgCl						

[a] A two liquid layer region extends from 0.7 to 17.6% of silver chloride, in equilibrium with solid phase xAlCl$_3$,yAgCl at 192.9°.

Barium Chloride

% $BaCl_2$	1.40	20.1	22.8	27.1
Temp. (°C)	192.5[a]	198.8	200.4	255.5
Solid phase		2AlCl$_3$,$BaCl_2$(?)		

[a] A two liquid layer region extends from below 2.0 to 13.0% of barium chloride, in equilibrium with solid phase 2AlCl$_3$,$BaCl_2$(?) at 191.5°.

Magnesium Chloride

% $MgCl_2$	9.5	12.4	15.4	17.9	22.1	27.5	29.1	30.9
Temp. (°C)	188.6	187.4	186.4	188.0	207.6	224.2	227.4	> 350.0
Solid phase		$AlCl_3$			2AlCl$_3$,$MgCl_2$(?)			$MgCl_2$

Mercurous Chloride

Work on this system had to be abandoned, since blackening of the mercurous chloride in bulbs containing low percentages and violent explosions in bulbs containing larger amounts prevented the determination of exact freezing points. Solubility is certainly only slight, and it is probable that no isolable compounds are formed.

Mercuric Chloride

% $HgCl_2$	3.0	7.7	18.5	26.4	32.8	37.4	41.4	48.2	55.9
Temp. (°C)	190.0	189.7	189.0	184.6	177.5	167.5	167.4	151.3	192.0
Solid phase				$AlCl_3$					
	58.1	63.2	70.9	82.6	90.0				
	200.5	216.2	238.1	259.7	272.1				
			$HgCl_2$						

Thallous Chloride

% TlCl	0.52	0.90	15.6	18.7	21.8	26.1	28.2	29.2	31.4
Temp. (°C)	189.4	189.9[a]	190.2	182.3	172.8	158.8	160.5	162.9	172.6
Solid phase	$AlCl_3$		xAlCl$_3$,yTlCl				2AlCl$_3$,TlCl(?)		
	33.1	34.2	37.9	42.1	46.2	51.2	53.5	55.5	56.5
	196.6	211.4	248.1	274.1	290.0	295.5	288.1	325.0	360.0
	AlCl$_3$,TlCl							TlCl	

[a] A two liquid layer region extends from 1.2 to 14.7% of thallium chloride, in equilibrium with solid phase xAlCl$_3$,yTlCl at 192.0°.

Stannous Chloride

(m.p. 246.8°)

% $SnCl_2$	0.98	1.11	15.3	18.1	22.1	28.5	30.7	33.5	38.8
Temp. (°C)	191.0	191.3	191.0[a]	188.2	187.0	204.4	207.4	209.1	195.0
Solid phase	$xAlCl_3,ySnCl_2$					$2AlCl_3,SnCl_2$			
	43.1	47.1	48.5	53.9	50.7	54.6	63.5	69.8	68.5
	178.6	164.1	158.7	136.9	158.2	153.3	142.3	135.4	138.3
	$2AlCl_3,SnCl_2$					$AlCl_3,SnCl_2$			
	70.9	75.0	86.1	90.8	100.0				
	154.3	176.3	223.4	235.7	246.8				
			$SnCl_2$						

[a] A two liquid layer region extends from 1.5 to 14.3% of stannous chloride, in equilibrium with solid phase $xAlCl_3,ySnCl_2$ at 192.0°.

Stannic Chloride

(b.p. 114°; f.p. 30.2°)

% $SnCl_4$	6.8	19.3	34.8	47.3	53.8	63.2	74.4	83.4	89.6
Temp. (°C)	188.6	182.6	174.2	167.8	164.5	158.3	150.0	139.5	130.9
Solid phase				$AlCl_3$					
	93.2	95.9	98.8	99.6	100.0				
	122.0	113.4	89.9	65.7	−30.2				
		$AlCl_3$			$SnCl_4$				

Antimony Chloride

% $SbCl_3$	3.6	17.1	21.9	32.2	41.4	46.7	52.2	59.5	64.2
Temp. (°C)	190.0	188.6	186.9	181.6	173.6	168.4	160.7	147.6	137.3
Solid phase				$AlCl_3$					
	74.4	77.0	84.8	92.5	95.9	100.0			
	112.9	106.1	83.0	69.9	71.1	73.4			

Chromic Chloride

No evidence of solution of or combination with chromic chloride was obtained.

Manganous Chloride

% $MnCl_2$	8.4	9.7	13.5	16.1	19.1	20.9	23.5	31.4	32.4
Temp. (°C)	190.0	189.9	186.4	185.4	197.2	203.9	212.9	226.9	271.1
Solid phase			$AlCl_3$			$2AlCl_3,MnCl_2$(?)			
	34.9								
	308.8								
	$MnCl_2$								

The data may be summed up as follows:

Compounds identified	m. p. (°C)	Two phase liquid system observed
$AlCl_3,LiCl$	143.5	no
$AlCl_3,NaCl$	....	yes
$AlCl_3,KCl$	....	yes
$AlCl_3,NH_4Cl$	304	yes
$AlCl_3,CuCl$	233	no
$AlCl_3,AgCl$	....	yes
$2AlCl_3,BaCl_2$	....	yes
$2AlCl_3.MgCl_2$	....	no
$2AlCl_3.TlCl$	....	yes
$AlCl_3.TlCl$	297	no
$2AlCl_3.SnCl_2$	209.3	yes
$AlCl_3.SnCl_2$	158.5	no
$2AlCl_3,MnCl_2$	....	no

It may be noted that several of the compounds reported by Baud could not be obtained by these authors. From their curves the eutectic temperatures may be obtained. They found no evidence of solid solutions in their work.

The factors influencing compound formation and solubility in the field of fused salts are:

The diversity factor: Metals much more electropositive and much more electronegative than aluminum provide the most complex and the most stable compounds.

The valence factor: Salts of monovalent metals with aluminum chloride form a greater number of complex compounds than salts of polyvalent metals; no complex compounds of quadrivalent metal salts with aluminum chloride could be prepared. The stability of the complexes is likewise comparable.

The unsaturation factor: If a metal can exist in more than one valence form the complexes produced from its lower valence salt are greater in number and more stable than those complexes formed from its higher valence salt. By comparing the number of and stability of complexes produced from salts of two metals where the valences are the same but one is unsaturated, the complexes of the unsaturated metal salt are more numerous and possess greater stability.

The position factor: If aluminum bromide is substituted for aluminum chloride the number, kind, and stability of the complexes are akin to those of the latter salt. However, by using salts of a metal which is lower in the electromotive series, such as antimony halides, the complexes formed are fewer and less stable.

The temperature factor: Since a difference of some 100° exists between the fusion points of aluminum chloride and aluminum bromide, their complexes have similar differences in melting point. Failure to isolate complexes of aluminum bromide undoubtedly are due to inability to secure temperatures low enough for crystallization. Stability of complexes from freezing point curves should not be compared unless these points are very near each other.

Internal pressure differences: In non-polar systems, solubilities or freezing point depression is dependent primarily upon the relative values of the internal pressure of the two components. As internal pressures diverge, solubility diminishes, and when the divergence is very large, two liquid layer systems may result. The results of this study divide the compounds into three classes: (1) The internal pressures of the two components are not markedly divergent, and their polarities only slight. Unless modified by compound formation, the solubility curves are essentially ideal with no apparent tendency toward incomplete miscibility in the liquid state. (2) Internal pressures are very widely divergent, the second component being a highly polar salt. This leads toward limited miscibility in the liquid state. When the two-liquid layer region extends over only a comparatively short composition interval an opposing effect is being exerted by extensive compound formation. (3) This class is

intermediate between the other two because the second component is a transition salt, and has a moderately greater internal pressure than the reference salt. Here the abnormal course of the freezing point curves indicates a strong tendency toward partial miscibility in the liquid state without actual appearance of a stable two liquid layer region. This is evidenced by a long, flat portion of the freezing point-composition curve.

The complexes containing lithium salts lie outside these three classes.

Molecular and atomic volumes: When the relative molecular radii differ appreciably, there is thought to be some influence toward immiscibility. However, atomic volumes appear to have more effect. Conductivity data are needed to determine the ion to which there is complex association.

The atomic number factor: Addition compound formation within a given periodic group increases with increasing atomic weight.

Eutectic and transition point data for the system $AlCl_3$-NaCl-KCl have been prepared [137]:

Eutectic Points				*Transition Points*			
Temp. (°C)	$AlCl_3$ (mol. %)	NaCl (mol. %)	KCl (mol %)	Temp. (°C)	$AlCl_3$ (mol. %)	NaCl (mol. %)	KCl (mol. %)
93	66	34	..	146	50	50	..
114	71	..	29	241	50	..	50
70	66	20	14	123	43.5	43.5	13
				110	54	31	15

The system of these three salts containing as high as 50 mole per cent of aluminum chloride at temperatures to 250° has also been studied.[138] The surface of the liquidus and isotherms through 25° was constructed. A ternary eutectic was obtained containing 16.5, 20.0, and 63.5 mole per cent of potassium chloride, sodium chloride, and aluminum chloride, respectively, and melting at 89°.

Plotnikov and Schvartzman [139] found no compound of aluminum chloride with antimony tribromide. The system is of the simple type with a eutectic at 8.39 mole per cent of aluminum chloride at 86°. They prepared the binary compound, $AlCl_3$.KBr, which has a melting point of 213°.

Plotnikov and Yakubson [140] found the heat of solution of aluminum chloride in molten alkali chlorides to be 77.97 Calories. The heats of formation in Calories of the binary compounds of aluminum chloride with the alkali halides were: $AlCl_3$.LiCl, 2.66; $AlCl_3$.NaBr, 3.28; $AlCl_3$,-KBr, 10.39. There is no exchange reaction in the systems (a) $AlCl_3$.NaBr and $AlCl_3$.KBr or (b) $AlBr_3$.NaCl and $AlBr_3$.KCl.

[137] L. Wasilewski, A. Kaczorowski, and M. Dynkin, *Przemysl Chem.*, **14**, 608-617 (1934); *C. A.*, **29**, 5728.

[138] V. A. Plotnikov and U. I. Shvartsman, *Mem. Inst. Chem. Acad. Sci. Ukrain.*, **3**, 387-400 (1936); *C. A.*, **31**, 6093. For a study of transference numbers in the system $AlCl_3$-NaCl, see also cu. V. Balmakov and V. I. Shelomov, *Trans. Leningrad Ind. Inst.*, 1938, No. 1, Sect. Met. No. 1, 36-49; *C. A.*, **34**, 928.

[139] V. A. Plotnikov and U. I. Schvartzman, *Mem. Inst. Chem. Ukrain. Acad. Sci.*, **4**, 137-153 (1937); *Brit. Chem. Abstracts-B*, 141 (1938).

[140] V. A. Plotnikov and S. I. Yakubson, *Mem. Inst. Chem. Ukrain. Acad. Sci.*, **4**, No. 2, 115-120 (1937); *C. A.*, **32**, 8250.

Table 2. Complexes of Aluminum Chloride with Organic Compounds

Compounds	Complex	Comment	Ref. No.
Ethylene+HCl	$AlCl_3.C_4H_8$		1, 111
Ethylene+benzene	$Al_2Cl_6.C_6H_4(C_2H_5)_2$	oily yellow liquid, b.p. 132–8°/9 mm.	2
Olefin ($RCH:CH_2$) + HCl	$RCH(Cl).CH_2.AlCl_2$		39
Benzene	$C_6H_6.Al_2Cl_6$		40, 41
Benzene	$C_6H_6.AlCl_3$		42
Benzene	complex formed		43
Benzene	none formed		5, 4
Benzene	$AlCl_3.3C_6H_6$	fuming liquid, very unstable	37, 44 9, 12, 11
Benzene+$HgCl_2$+Al	$C_6H_6.AlCl_3.HgCl$	hygroscopic (large transparent six-sided plates)	7, 46
Toluene+$HgCl_2$+Al	$C_7H_8.AlCl_3.HgCl$	hygroscopic	7
Ethylbenzene+$HgCl_2$+Al	$C_8H_5C_2H_5.AlCl_3.HgCl$	hygroscopic	7
Xylenes+$HgCl_2$+Al	$C_6H_4(CH_3)_2.AlCl_3.HgCl$	hygroscopic	7
Cumene+$HgCl_2$+Al		hygroscopic	7
Pseudocumene+$HgCl_2$+Al		hygroscopic	7
Mesitylene+$HgCl_2$+Al	$Al_2Cl_6.C_6H_3(CH_3)_3$	hygroscopic	7
Cymene+$HgCl_2$+Al		hygroscopic	7
Cymene	$Al_2Cl_6.3(C_{10}H_{14})$	sp. gr. 1.139/0°C.	8
Toluene	$AlCl_3.3C_7H_8$	fuming liquid, very unstable	9, 12, 44
Toluene	$Al_2Cl_6.6C_7H_8$	orange liquid, sp gr. 1.08/0°C	10, 11, 104
Toluene	none formed		4
Toluene	complex formed		43
Xylene	none formed		4
1,3,5-Triethylbenzene	$2AlCl_3.C_{12}H_{18}$		2, 3, 15
Benzene+alkyl or acyl halide	complex formed		109
Tetralin	$C_{10}H_{12}.AlCl_3$		110
Xylene and trimethylbenzene	$2AlCl_3.C_6H_4(CH_3)_2.3C_6H_3(CH_3)_3$		2
Triethylbenzene	$2AlCl_3.C_6H_3(C_2H_5)_3$	liquid, unstable	2, 8, 13, 14, 3
Triethylbenzene and benzene	$2AlCl_3.C_6H_3(C_2H_5)_3.6C_6H_6$		14
Triethylbenzene and toluene	$2AlCl_3.C_6H_3(C_2H_5)_3.5C_6H_5CH_3$		2, 15
Triethylbenzene and *m*-xylene	$2AlCl_3.C_6H_3(C_2H_5)_3.4C_6H_4(CH_3)_2$		15
Triethylbenzene and ethylbenzene	$2AlCl_3.C_6H_3(C_2H_5)_3.4C_6H_5C_2H_5$		2
Triethylbenzene and mesitylene	$2AlCl_3.C_6H_3(C_2H_5)_3.3C_6H_3(CH_3)_3$		2, 15
Triethylbenzene and propylbenzene	$2AlCl_3.C_6H_3(C_2H_5)_3.3C_6H_5C_3H_7$		2
Triethylbenzene+triisopropyl benzene and hydrogen chloride	$2AlCl_3.C_6H_3(C_2H_5)_3.C_6H_3[CH(CH_3)_2]_3.HCl$	yellow crystals	14
Triethylbenzene and hydrogen chloride	$2AlCl_3.2C_6H_3(C_2H_5)_3.HCl$	yellow crystals, m.p. 48–49°	13, 14, 115
Triethylbenzene and tetraethylbenzene	$2AlCl_3.C_6H_3(C_2H_5)_3.3C_6H_2(C_2H_5)_4$		2

Table 2.—*Continued*

Compounds	Complex	Comment	Ref No.
Triisopropylbenzene	$2AlCl_3.C_6H_3[CH(CH_3)_2]_3$	unstable	13, 14
Triisopropylbenzene and benzene	$2AlCl_3.C_6H_3[CH(CH_3)_2]_3.C_6H_6$	green liquid	13, 14
	$2AlCl_3.C_6H_3[CH(CH_3)_2]_3.6C_6H_6$	liquid	
Triisopropylbenzene and hydrogen chloride	$2AlCl_3.2C_6H_3[CH(CH_3)_2]_3.HCl$	yellow crystals, unstable	13, 14
Triisobutylbenzene and hydrogen chloride	$2AlCl_3.2C_6H_3[CH_2CH(CH_3)_2]_3.HCl$	yellow crystals, unstable	13
Hexaethylbenzene	$2AlCl_3.C_6(C_2H_5)_6$	colorless crystals	48, 3
Alkyl halides	$(AlCl_4)^- + alkyl^+$		113
Ethyl bromide	$Al_2Cl_6.C_2H_{10}$		15
Isobutyl chloride		45.9% Cl	1
Chloroform	$AlCl_3.CHCl_3$	hygroscopic gummy mass	32
Methyl chloride + Al + $AlCl_3$	$Al(CH_3)_2Cl$ and $Al(CH_3)Cl_2$		33
Chlorobenzene	none formed		31
Chlorobenzene	complex formed		43
Bromobenzene	$Al_2Cl_6C_6H_5$		31
Bromobenzene	complex formed		43
Iodobenzene	$Al_2Cl_6C_6H_5$		31
Triphenylchloromethane + Al metal	addition compound with $AlCl_3$		34
Triphenylchloromethane	$AlCl_3.C_{19}H_{15}Cl$		32, 58, 114
Benzene and isopropyl bromide	$Al_2Br_3C_6H_3[CH(CH_3)_2]_3$		2
Benzene and ethyl chloride	$Al_2Cl_6.s\text{-}C_6H_3(C_2H_5)_3$	oily, yellow liquid, b.p. 132-8°/9 mm.	2, 3, 15
Benzene and ethyl chloride	$Al_2Cl_6C_6(C_2H_5)_6$		2
Benzene and ethyl bromide	$[Al(C_2H_5Br)_6][C_6(C_2H_5)_6](AlBr_4)_3$		35
p-Nitrobenzyl chloride	$AlCl_3.C_7H_6O_2NCl$		60
Nitrobenzyl chloride	$AlCl_3.C_6H_4(CH_2Cl)NO_2$		61, 62
Benzyl chloride	$C_6H_5.AlCl_2$		63
Acetyl chloride	$Al_2Cl_6.(C_2H_3O)_4$		16
Acetyl chloride	$AlCl_3.CH_3COCl$	in carbon disulfide	17
Acetyl chloride	$Al_2Cl_4.[O.CCl_2.CH(COCH_3)_2]_2$	hydrolyzed by water to ethyl acetylaceto acetate	20
Acetyl chloride	$Al_2Cl_6C_{12}H_{14}O_6$		23
Acetyl chloride	$AlCl_3.CH_3COCl$	yellow syrup	21
Monochloroacetyl chloride	$AlCl_3.CH_2ClCOCl$	hygroscopic crystals	18
α:β:β:β'-Tetrachloropropionyl chloride	resinous product		18
Trichloroacrylyl chloride	$AlCl_3.CCl_2{:}CCl.COCl$		22
Aliphatic acid chlorides	$AlCl_3.RCOCl$ or $(AlCl_4)CO.R$		50
RCOCl	$AlCl_3.RCOCl$		17
RCOCl	$Al_2Cl_6.(RCOCl)_2$	function of $AlCl_3$	24
$(RCOCl)_2Al_2Cl_6 + C_nH_n$	$Al_2Cl_6.(RCO.C_mH_{m-1})_2$	crystalline	24
Carbamyl chloride	$NH_2.COCl.AlCl_3$		112

Table 2—*Continued*

Compounds	Complex	Comment	Ref No
Benzamide	$C_6H_5CONHAlCl_2$		117
Substituted carbamyl chlorides			26, 25, 112
Chlorofumaryl chloride	none formed, only resinous product		18
Benzoyl chloride	$AlCl_3 \cdot C_6H_5COCl$	long colorless needles, m.p. 93°	27, 29
Benzoyl chloride	$AlCl_3 \cdot C_6H_5COCl$		51-3, 54, 66
Benzoyl chloride	$AlCl_3 \cdot C_6H_5COCl$	reaction velocity study	65
Benzoyl chloride	$AlCl_3 \cdot C_6H_5COCl$	eutectic 1 6.53= $AlCl_3$ BzCl	29
Benzoyl chloride	$C_6H_5CCl_2O \cdot AlCl_3$		55
Benzoyl chloride	$Al_2Cl_6(C_6H_5COCl)_3$	large colorless lamellae	19
Benzoyl chloride	$AlCl_3 \cdot C_6H_5COCl$	molecular weight study	30
Phthaloyl chloride	$Al_2Cl_6(C_6H_4C_2O_2Cl_2)$	discussion	19
Terephthalyl chloride			28
m-Nitrobenzoyl chloride	$AlCl_3 \cdot C_7H_4O_3NCl$		52
p-Nitrobenzoyl chloride	$AlCl_3 \cdot C_7H_4O_3NCl$		52
Benzoyl chloride and benzene	$C(C_6H_5)_2Cl_2O \cdot AlCl_3$		55
Aromatic acyl halides	$RCOCl \cdot AlCl_3$		52
Aromatic acyl halides +aromatic hydrocarbon	$RCOR' \cdot AlCl_3$		52
Acetone	$AlCl_3(C_3H_6O) \cdot AlCl_3 \cdot 2C_3H_6O$	m.p. 116°	36
Acetone	$3AlCl_3 \cdot 5C_3H_6O$	contains Cl^- and $(Al_6Me_2C(O))^{+++}$ ions	64
Benzophenone	$AlCl_3 \cdot (C_6H_5)_2CO$		52, 54, 65, 66
Benzophenone	$AlCl_3 \cdot (C_6H_5)_2CO$	in molecular weight study	30
Benzophenone	$AlCl_3 \cdot (C_6H_5)_2CO$	long yellow needles, m.p. 130 °C	69
Acetophenone	$Al_2Cl_6 \cdot 2C_6H_5COCH_3$		28
Acetophenone	$AlCl_3 \cdot C_6H_5COCH_3$	crystallizes slowly and resinifies	69
Benzene and $CH_3COCl.AlCl_3$	$AlCl_3 \cdot C_6H_5COCH_3$	m.p. 64 °C	21, 52
Benzene+acyl halide $AlCl_3$ complex	$AlCl_3 \cdot RCOC_6H_5$		17
Toluene+ $CH_3COCl.AlCl_3$	$AlCl_3 \cdot C_7H_7COCH_3$	prep of acetyl compds.	21, 52
Xylene+ $CH_3COCl.AlCl_3$	$AlCl_3 \cdot C_8H_9COCH_3$	prep of acetyl compds	21, 52
Anthraquinone	$Al_2Cl_6 \cdot C_{14}H_8O_2$		28
Benzoylmesitylene		crystals	71
Acid chlorides+ anthracene			71
Acid chlorides+ phenanthrene			71
5-Benzoyl-acenaphthene	$AlCl \cdot C_{19}H_{14}O$		71, 72

Table 2.—*Continued*

Compounds	Complex	Comment	Ref. No.
2-Benzoylfluorene	$AlCl_3.C_{20}H_{14}O$		71, 73
Acid chlorides+ stilbene			71
Acid chlorides+ diphenylnaphthalene			71
Acid chlorides+ mesitylene			71
Acid chlorides+ retene		m.p. 114°	71
Benzoyl chloride+ biphenyl	$(C_6H_5CO.C_6H_4.C_6H_5)_2Al_2Cl_8$	large, yellow needles	19
Benzoyl chloride+ retene	$(C_6H_5CO.C_{18}H_{17})_2Al_2Cl_8$	red crystals	19, 74
Phenyl tolyl ketone +ferric chloride	$C_6H_5CO.C_6H_4CH_3.AlCl_3.FeCl_3$		57
α-Benzoyl-β-naphthol	$AlCl_3.C_{17}H_{12}O_2$		74
α-Benzoyl-β-naphthol		golden yellow	19
Phthaloyl chloride+ aromatic hydrocarbons			19
Butyryl chloride+ aromatic hydrocarbons			19
2,3-Dibromoanthraquinone		very stable, yellowish micro crystals	70
3,10-Perylenequinone			70
Phenanthrenquinone	$AlCl_3.C_{14}H_8O_2$		67
3-Nitrobenzophenone	$AlCl_3C_{13}H_9O_3N$		52
4-Methylbenzophenone	$AlCl_3.C_{14}H_{12}O$		52
3'-Nitro-4-methylbenzophenone	$AlCl_3.C_{14}H_{11}O_3N$		52
4'-Nitro-4-methylbenzophenone	$AlCl_3.C_{14}H_{11}O_3N$		52
Benzoylbiphenyl	$Al_2Cl_8.(C_{13}H_{14}O)_2$		19, 74
4-Methoxybenzophenone	$AlCl_3.C_{14}H_{12}O_2$		52
3'-Nitro-4-methoxybenzophenone	$AlCl_3.C_{14}H_{11}O_4N$		52
4'-Nitro-4-methoxybenzophenone	$AlCl_3.C_{14}H_{11}O_4N$		52
Conc. formic acid	$Al_2Cl_2(CHO_2)_4.2CH_2O_2.5H_2O$	soluble in conc. acid at 60 °C	118
Acetic acid	$4AlCl_3.CH_3COOH$	discussion	75
Acetic acid (glacial)	$2Al_2Cl_2(C_2H_3O_2)_4$ and $Al_2Cl_4(C_2H_3O_2)_2.15H_2O$		118
Acetic acid	$AlCl_3.2Al(OOCCH_3)_3$		38
Acetic anhydride+ ether	$(C_2H_5)_2O.2AlCl[OOCCH_3]_2$		79
Propionic acid	$Al_2Cl_2(C_3H_5O_2)_4$		118, 29
Acetic acid+ chloral	$Al_2Cl(OOCCH_3)_5.CCl_3CHO$		76
Diphenylphthalide	$C_{20}H_{12}O_2.AlCl_3$	crystals stable to 300°	77
o-Benzoylbenzoic acid	$C_{14}H_9O_3.Al_2Cl_6$		78
Ethyl oxalate	$AlCl_3.C_6H_{10}O_4$		75
Ethyl malonate	$AlCl_3.CH_2(COOC_2H_5)_2$		75
Ethyl benzoate	$Al_2Cl_8.(C_6H_5COOC_2H_5)_2$		84
Ethyl benzoate	$AlCl_3.C_6H_5COOC_2H_5$		75

Table 2.—*Continued*

Compounds	Complex	Comment	Ref. No.
Phenyl benzoate	$AlCl_3.C_{13}H_{10}O_2$		85, 51
Methyl mandelate	$4AlCl_3.C_9H_{10}O_3$		75
Methanol	$AlCl_3(OCH_3).2AlCl_3.16CH_3OH$	in absolute ether white, crystalline, unstable when heated	36
Methanol	$AlCl_3.4CH_3OH$		80
Methanol	$AlCl_3.6CH_3OH$		80
Methanol	$Al_2Cl_6.10CH_3OH$		45
Methanol	$Al_2Cl_4(OCH_3)_2$		45
Methanol	none formed	a violent reaction ensues	92
Ethanol	$AlCl_2(OC_2H_5).2AlCl_3.10C_2H_5OH$		36
Ethanol	$Al_2Cl_6.8C_2H_5OH$		45
Ethanol	$Al_2Cl_3.(OC_2H_5)_3$		45
Ethanol	$C_2H_5O.AlCl_2$		56
Ethanol	none	a violent reaction ensues	92
Aluminum ethoxide	$AlCl_3.3Al(OC_2H_5)_3$	used for ester condensation	86
Aluminum ethoxide	(?)		96
Aluminum ethoxide	$AlCl_3.(C_2H_5O)_3Al$		45
n-Propanol	$AlCl_3(OC_3H_7).2AlCl_3.5C_3H_7OH$		36
n-Propanol	$AlCl_3.3C_3H_8O$		49
n-Propanol	$Al_2Cl_6.nC_3H_7OH$; $Al_2Cl_4.(OC_3H_7)_2$		45
Propanol	$2AlCl_3.5C_3H_7OH$		80
Aluminum propoxide			96
Dichlorohydrin	$Al_2Cl_6(O:C_3H_6Cl_2)_2$	crystalline, hygroscopic	68
Butanol	$Al_2Cl_6.4C_4H_9OH$		45
Butanol	$Al_2Cl_4.(OC_4H_9)_2$		45
Butanol	$AlCl_3.3C_4H_{10}O$		49
Isoamyl alcohol	$2AlCl_3.5C_5H_{11}OH$		80
Isoamyl alcohol	$Al_2Cl_4.(OC_5H_{11})_2$		45
Isoamyl alcohol	$Al_2Cl_6.n(C_5H_{11}OH)$		45
Allyl alcohol+ methanol	$AlCl_3.C_3H_6O.CH_4O$		97
Phenols	$ArO.AlCl_2$		59
Phenol	$Al_2Cl_3(OC_6H_5)_3$	yellow powder, readily soluble in CS_2	68
Phenol	$C_6H_5O.AlCl_2$		56
Resorcinol	$Al_2Cl_4C_6H_4O_2$	thick, reddish-brown liquid	68
Diethyl ether	$Al_2Cl_6.2(C_2H_5)_2O$		54, 75
Diethyl ether	$Al_2Cl_6.2(C_2H_5)_2O$	molecular weight determination	30
Diethyl ether	$AlCl_3.2(C_2H_5)_2O$	m.p. 33-35°, colorless plates, completely decompose at 106°	81
Di-*n*-propyl ether	$Al_2Cl_6.2[(C_3H_7)_2O]$	red liquid	81
Phenyl ether	$Al_2Cl_6.2(C_6H_5)_2O$		28
Phenetole	none formed		75
Anisole	$Al_2Cl_6.2C_6H_5OCH_3$		28
Anisole	$AlCl_3.C_6H_5OCH_3$	study of $AlCl_3$ compounds with organic subs. containing O_2	75, 82
Diphenyl sulfide	complex formed	yellow precipitate	83

Table 2.—*Continued*

Compounds	Complex	Comment	Ref. No.
Nitrobenzene	$Al_2Cl_6.2C_6H_5NO_2$		54, 88, 106-108, 116
Nitrobenzene	$AlCl_3.2C_6H_5NO_2$	colorless, highly hygroscopic rhombic plates, m. 25.5°C.	105
Nitrobenzene	$AlCl_3.2C_6H_5NO_2$	rhombic plates, m. 30.5°C.	53
Nitrobenzene	$AlCl_3.C_6H_5NO_2$	pale yellow needles, m. 90°C.	105
Nitrobenzene	$AlCl_3.C_6H_5NO_2$		53, 116
Nitrobenzene	complex formed	crystals	30
m-Dinitrobenzene	$AlCl_3.C_6H_4(NO_2)_2$		75
o-Nitrotoluene	$AlCl_3.CH_3C_6H_4NO_2$		75
o-Nitrotoluene	$AlCl_3.2CH_3C_6H_4NO_2$	yellow plates, decompose at 55.1°C.	105
o-Nitrotoluene	$AlCl_3.CH_3C_6H_4NO_2$	highly hygroscopic, yellow needles, m.p. 99.5°C.	105
m-Nitrotoluene	$AlCl_3.2CH_3C_6H_4NO_2$	straw-yellow plates, transition point 35°C.	105
m-Nitrotoluene	$AlCl_3.CH_3C_6H_4NO_2$	bundles of needles, m.p. 99.5°C.	105
p-Nitrotoluene	$AlCl_3.CH_3C_6H_4NO_2$	very long plates, m.p. 109°C	105
o-Chloronitrobenzene	$AlCl_3.ClC_6H_4NO_2$	yellow hygroscopic needles, m.p. 89°C.	53, 105
m-Chloronitrobenzene	$AlCl_3.ClC_6H_4NO_2$	golden yellow hygroscopic needles, m.p. 104°C.	105
m-Chloronitrobenzene	two compounds		53
p-Chloronitrobenzene	$AlCl_3.ClC_6H_4NO_2$	straw-yellow plates, m.p. 126°C.	105
o-Bromonitrobenzene	$AlCl_3.BrC_6H_4NO_2$	m.p. 100°C.	105
m-Bromonitrobenzene	$AlCl_3.BrC_6H_4NO_2$	long colorless needles, m.p. 116°C.	105
p-Bromonitrobenzene	$AlCl_3.BrC_6H_4NO_2$	yellow needles, m.p. 145°C.	105
4-Nitrodiphenylmethane	$AlCl_3.C_{13}H_{11}O_2N$		60
Benzene + nitrosyl chloride	$2AlCl_3.3C_6H_6.3NOCl$		103
Aniline + HCl	$AlCl_3.3(C_6H_5NH_2.HCl)$	study of double salts of aniline; white rectangular crystals	87
Pyridine		crystalline	88
Benzeneazo-*p*-phenol		study of valency of halides	89
Acetonitrile	$2AlCl_3.C_2H_3N$	white crystalline powders	90
Acetonitrile	$AlCl_3.C_2H_3N$		91
Acetonitrile	$AlCl_3.2C_2H_3N$		74
Chloroacetonitrile	$2AlCl_3.C_2H_2NCl$	crystalline, m.p. 38°	90

Table 2.—*Concluded*

Compounds	Complex	Comment	Ref. No.
Trichloroacetonitrile	$2AlCl_3.C_2NCl_3$	white crystalline, unstable when heated	90
Propionitrile	$2AlCl_3.C_3H_5N$	m.p. 95°	91, 74
Propionitrile	$AlCl_3.C_3H_5N$	m.p. 70-80°	74, 91
Propionitrile	$AlCl_3.2C_3H_5N$	m.p. 58-60°	74, 91
Diphenyl sulfone	$AlCl_3.C_{12}H_{10}O_2S$		52, 94, 95
4-Bromodiphenyl sulfone	$AlCl_3.C_{12}H_9O_2BrS$		93, 95
Phenyl *p*-tolyl sulfone	$AlCl_3.C_{13}H_{12}O_2S$		52, 94, 95
4-Methoxydiphenyl sulfone	$AlCl_3.C_{13}H_{12}O_3S$		52
Methylsulfonyl chloride	$AlCl_3.CH_3O_2ClS$		98
Ethylsulfonyl chloride	$AlCl_3.C_2H_5SO_2Cl$		98
Benzenesulfonyl chloride	$AlCl_3.C_6H_5O_2ClS$		52, 95, 88
p-Chlorobenzenesulfonyl cchloride	resinous products		18
p-Chlorobenzenesulfonyl chloride	$AlCl_3.C_6H_4O_2Cl_2S$		94
p-Bromobenzenesulfonyl chloride	$AlCl_3.C_6H_4O_2ClBrS$	crystals, stable < 150 C.	18, 93, 43
m-Nitrobenzenesulfonyl chloride	$AlCl_3.C_6H_4O_4NClS$		66
p-Toluenesulfonyl chloride	$AlCl_3\ C_7H_7O_2ClS$		94
$AlCl_3.SO_2Cl$+benzene	$AlCl_3.SO_2.C_6H_5$		100
Phenyldichloroarsine	$(C_6H_5)AsCl_2.AlCl_3$	pale yellow crystals	99
Arsenious chloride and acetylene	$Al[(CHCl.CHCl.AsCl_2)(CHCl.CHCl)_2AsCl]$ and $Al(CHCl.CHCl.AsCl_2)_3$		102
N_2O_4 and chlorobenzene	$2AlCl_3.3C_6H_5Cl.3N_2O_4$		101

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Chapter 4

Mechanism of Reactions Catalyzed by Anhydrous Aluminum Chloride

Introduction

The evolution of theories concerning the mechanism of reactions catalyzed by aluminum chloride follows the growth of conceptions of the role of catalysts in organic chemistry. Friedel and Crafts assumed the formation of intermediate compounds with aluminum chloride because at that time catalytic phenomena were assumed to occur by primary formation of a complex compound of the catalyst with either or both reactants. It soon became apparent, however, that in many catalyzed reactions, complex formation could not be noted. In other instances it was observed that reactions in which complexes were formed were retarded rather than accelerated. The existence of complexes, therefore, did not explain the mechanism by which reaction occurred.

Consequently, there arose a new conception of the role of catalysts in organic chemistry. The catalyst was assumed to exert its effect only by activating the reactants In reality, the activation theory was merely a refutation. It was a logical negative response to the interpretation of catalytic activity solely on the basis of the formation of intermediate catalyst complexes. Heat, alone, was shown to effect numerous reactions which had been previously considered as proceeding only under the influence of catalysts. In these cases the formation of intermediate complexes obviously was not a contributing factor to reaction. The activation theory thus indicates only the apparent raising of the energy level of one or both reactants due to excitation upon contact with the catalyst. It does not explain the manner in which the excitation is induced.

Currently, proponents of both schools of thought have used electronic concepts as a visual means of portraying their theories. The fact that aluminum chloride forms complexes with many compounds is readily explained by the fact that aluminum chloride, having an incomplete octet, is electron deficient, and thus unites with any compound which has an unshared pair of electrons. Additional explanation is necessary, however, to explain the role of all these complexes in reactions catalyzed by aluminum chloride.

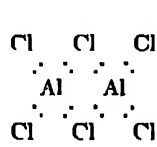
Attempts to explain the disproportionating effect of aluminum chloride are comparatively recent. Of necessity such studies involve the tracing of ionic changes and electromeric deformations in molecules of one or both reactants. Here a number of investigators have found it convenient to accept complexes postulated by earlier investigators, interpreting their activity or non-activity through the octet theory. Others

have assumed unexplained temporary deformation of the benzene ring, postulating a resonance form which acts as acceptor for any satisfactorily ionized particle present. Although there is no definite proof of the existence of such deformed rings during Friedel-Crafts reactions, catalyzed aromatic halogenation has been shown to proceed in this way. Electromeric changes play a decisive role in orientation and reactivity in aromatic substitution.

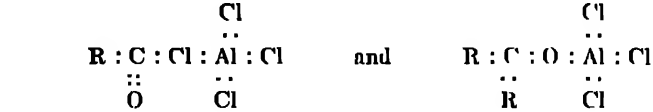
At the present time the activation theory, as seen in the light of electronic conceptions, most satisfactorily explains the manifold activities of aluminum chloride in organic chemistry. Since it is still in an embryo stage, however, much investigation of a physico-chemical nature is required to substantiate its applicability to all reactions catalyzed by aluminum chloride. X-ray studies of the benzene molecule directed at revealing it in a suitably excited state may do much to clear up the now rather vague ideas of catalyzed electromeric changes in the benzene ring.

Complex Formation in the Light of the Octet Theory

The tendency of aluminum chloride to form complexes is best evidenced by the fact that it exists as the dimer, Al_2Cl_6, which can be represented as:



The greater stability of the dimer over that of the electron-deficient monomer is undoubtedly due to the existence of several resonance forms of Al_2Cl_6 which contribute to its stability On the basis of the foregoing electronic structure it would be expected that only monomeric aluminum chloride forms complexes with organic compounds However, in the Friedel-Crafts reaction, complexes have been assumed to occur between $AlCl_3$ or Al_2Cl_6 with either or all of the components involved—the aromatic hydrocarbon, the organic halide, and the reaction product The existence of complexes of the types



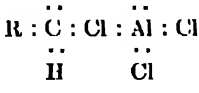
and

has been proved; they are stable, well-characterized products However, the fact that aluminum chloride does form stable complexes with acyl halides and with ketones does not explain the catalytic activity of the metal halide in Friedel-Crafts ketone synthesis. These complexes, which are very stable products, hinder rather than accelerate reaction

The existence of complexes of aluminum chloride with aromatic hydrocarbons and hydrogen halide, but not of aluminum chloride with the

aromatic hydrocarbon alone, has been indicated.[1] Several investigators[2] have shown, by cryoscopic studies, that there is evidence of complex formation when benzene is treated with aluminum chloride or bromide in the presence of hydrogen halide, but the assigned empirical formulas, for example, $Al_2Cl_6,6C_6H_6$ and $Al_2Br_6,C_6H_5CH_3$, do not signify the presence of hydrogen chloride in the complex. Other workers[3] show, also by cryoscopic studies, that aluminum bromide forms no complex with aromatic hydrocarbons, alone, but that in the presence of hydrogen halide molecular compounds, in which the hydrogen halide is bound, are probably formed. Later,[4] conductivity studies were reported to indicate the formation of complexes of aluminum chloride and aromatic hydrocarbons, alone; but these observations were made on the increased conductivity noted upon addition of alkyl halide to benzene in the presence of aluminum chloride *before evolution of hydrogen halide occurred*, and hence cannot be considered as reliable evidence for the formation of aluminum chloride-aromatic hydrocarbon complexes. Hydrogen halides have been shown[1] to have a decided influence on the conductivity of a mixture of toluene and aluminum bromide. Contrary to assumptions of early investigators* more recent physico-chemical data[5] practically negate the existence of aluminum chloride-aromatic hydrocarbon complexes.

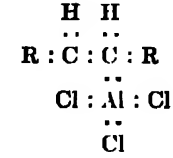
Increase in conductivity has been noted upon addition of aluminum chloride to alkyl halides.[6] Here too association or complex formation is indicated, provided of course (1) that the aluminum chloride used was absolutely anhydrous and (2) that the rise in conductivity observed was not due to dehydrohalogenation of the alkyl halide and subsequent complex formation of the resulting olefin with aluminum chloride. With respect to these provisions, it should be pointed out that it is very difficult to render aluminum chloride entirely anhydrous, and that in the course of the conductivity studies mentioned above, evolution of hydrogen chloride was noted upon addition of aluminum chloride to the alkyl halides. If alkyl halides do form complexes with aluminum chloride they may be regarded as having the following electronic structure:



Ionization of this complex, producing a positive alkyl ion, can explain subsequent reactivity.

[1] J. F. Norris and J. E. Wood, *J. Am. Chem. Soc.*, 62, 1428-1432 (1940); see also page 97.
[2] G. Gustavson, *Bull. soc. chim. (2)*, 30, 435 (1878); *J. Russ. Chem. Soc.*, 12, 1-2 (1880); *C. Z.*, 1880, 584; *J. prakt. Chem. (2)*, 42, 501-507 (1890). J. F. Norris and D. Rubinstein, *J. Am. Chem. Soc.*, 61, 1163-1170 (1939).
[3] B. Menschutkin, *J. Russ. Phys.-Chem. Soc.*, 41, 1089-1110 (1909); *C. Z.*, 1910, I, 167. I. Kablukow and A. Saschanow, *J. Russ. Phys.-Chem. Soc.*, 41, 1755-1762 (1909); *C. Z.*, 1910, I, 912.
[4] J. W. Walker, *J. Chem. Soc.*, 85, 1082-1098 (1904).
* See page 97.
[5] E. Wertyporoch and T. Firla, *Z. physik. Chem.*, 162, 398-414 (1932); see also p. 103.
[6] J. W. Walker, *loc. cit.* E. Wertyporoch and T. Firla, *loc. cit.* also see page 31.

Olefins form highly active complexes with aluminum chloride; a carbon atom having an incomplete octet accounts for the instability and reactivity of the product

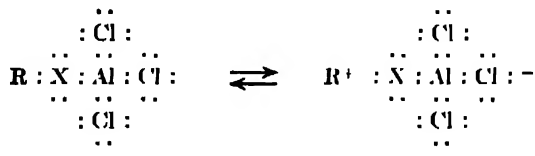


Complex formation has been assumed to take place between the positive nucleus of the central atom of the catalyst and one of the alternate carbon atoms of the benzene ring, which, according to Lowry's theory [7] have a complete octet of electrons; and it has been postulated that the hydrogen atom attached to the carbon in question is caused to become labile.[8]

Walker [9] and Dougherty [10] have found that metathetical reactions occur between certain types of aliphatic halogen compounds in the presence of aluminum chloride. On this basis, the latter investigator suggests that ionization of an alkyl halide is induced by aluminum chloride:

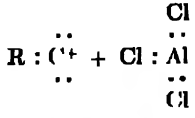
$$RX + AlCl_3 \rightleftarrows RX \cdot AlCl_3 \rightleftarrows R^+(XAlCl_3)^-$$

or,



Such an ionization harmonizes with the theory of Prins,[11] who assumed that aluminum chloride polarizes or ionizes benzene in such a way that it produces a phenyl ion and a hydrogen ion. The Friedel-Crafts reaction may thus be regarded as a reaction of the negative phenyl ion with the positive alkyl ion.

Rearrangement of alkyl halides by aluminum chloride may be explained by Whitmore's theory of rearrangement [12]: assuming an ionized complex of aluminum chloride with alkyl halide,



[7] T. M. Lowry, *J. Chem. Soc.*, 123, 822-831 (1923).
[8] B. V. Tronow, L. V. Ladigina, and I. M. Karpenko, *J. Gen. Chem. Russ.*, 1, 910-916 (1931); *Brit. Chem. Abstracts-A*, 373 (1932).
[9] J. W. Walker, *J. Chem. Soc.*, 84, 1082-1098 (1904).
[10] G. Dougherty *J. Am. Chem. Soc.*, 51, 576-580 (1929).
[11] H. J. Prins, *Chem. Weekblad*, 24, 615 (1927).
[12] F. C. Whitmore, *J. Am. Chem. Soc*, 54, 3274-3283 (1932).

the electron deficiency in the alkyl ion migrates from a primary to a secondary to a tertiary carbon atom.

Price and Ciskowski [13] believe that reactions of the olefins may be accounted for also on the basis of the electron affinity of aluminum chloride, with the formation of a molecule having a carbon atom deficient in a pair of electrons. They assumed that this complex was, therefore, able to react with a benzene ring However, since aluminum chloride catalyzes nuclear condensation of aromatic compounds, as in the Scholl reaction,* a direct activation of the benzene ring must also be assumed.

It has been shown that aluminum chloride catalyzes interchange of hydrogen. When benzene and hydrogen chloride containing 13.4 per cent deuterium chloride are brought together in contact with aluminum chloride at 25° and 50°, over 90 per cent of the deuterium passes to the benzene. Although a similar exchange occurs in the absence of catalyst, it is much slower.[14] The reaction has been extended [15] to the production of deuteriobenzene, C_6D_6, containing up to 98 per cent of the theoretical amount of deuterium. It has been shown that in the deuteration of phenol and of aniline the deuterium enters only the *ortho* and *para* positions, the *meta* position remaining unaffected.[16] Deuteration may thus be regarded as an electrophilic aromatic substitution in which deuterium is a cation which reacts at the negatively charged carbon atoms. If analogy is made to alkylations with alkyl halides, the alkyl group is a cation which undergoes similar reaction with benzene.

Meerwein [17] and Hückel [18] consider addition compounds of aluminum chloride with acyl halides to be coördination compounds, of the type:

$$(RCO)^+(AlCl_4)^-$$

Fairbrother [19] has shown experimentally by the use of radioactive aluminum chloride that an interchange of chlorine atoms takes place between acetyl chloride and aluminum chloride. Since the interchange occurred in the absence of any third reactant or evolution of hydrogen chloride, he assumed that there was a conversion of the covalent carbon-chlorine bond into an ionic bond:

$$CH_3COCl + AlCl_3 \longrightarrow (CH_3CO)^+ + (AlCl_4)^-$$

The interchange, however, does not prove that the acyl halide complex actually undergoes ionization. Wertyporoch and Firla [20] have shown by conductivity measurements that the addition of aluminum chloride to acetyl or benzoyl chloride results in proportionate lowering of the molar conductivity of these acid halides

* See Chapter 13.

[13] C. C Price and J. M Ciskowski, *J. Am Chem Soc*, 60, 2499-2502 (1938)

[14] J Kenner, M. Polanyi, and P Szego, *Nature*, 135, 267-268 (1935) C 4, 29, 2443.

[15] A. Klit and A. Langsteth, *Z physik. Chem*, A176, 65-80 (1936) C 4, 30, 5091

[16] A. P Best and C. L. Wilson *J. Chem Soc*, 28-29 (1938), *cf* C K Ingold, C G Raisin, and C L. Wilson, *J. Chem. Soc*, 1637-1643 (1936)

[17] H. Meerwein, *Ann.*, 455, 227-253 (1927), H. Meerwein and W Burneleit *Ber*, 61, 1840-1847 (1928)

[18] W. Huckel, "Theoretische Grundlagen der Organischen Chemie," Vol 1, p 351 1931

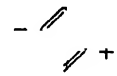
[19] F Fairbrother, *J Chem. Soc*, 503-506 (1937)

[20] E Wertyporoch and E. T. Firla, *Z. physik Chem*, 162, 398-414 (1932), see also page 35 of this book.

The fact that alkyl halides undergo rearrangement in Friedel-Crafts reactions, whereas no branching occurs in Friedel-Crafts reactions with acyl halides may thus be explained by the differences in ionization of the aluminum chloride complexes formed. Although the compound with acyl halides has been shown to be $(CH_3CO)(AlCl_4)$, it is not ionized. No dissociation occurs with formation of an acyl ion having an electron deficiency; and hence the Friedel-Crafts reaction with acyl halides proceeds *without rearrangement of the carbon chain.*

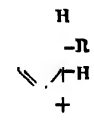
Electromeric Shifts and Orientation

The activation of an aromatic nucleus by aluminum chloride may be regarded as a distortion of the stable benzene ring into a form which facilitates substitution. Such a distorted molecule may, indeed, be considered as a temporarily stable resonance form of benzene as yet unidentified:

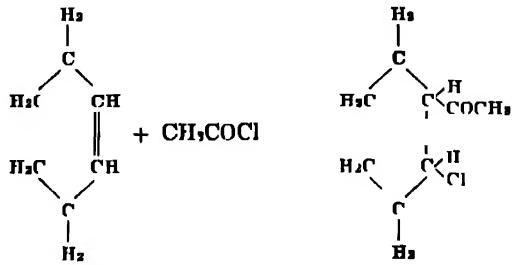


Indications are that it may unite with the adjunct to form a free radical of the type:

or an ion:



It may be postulated that acyl ions add to the double bond of the aromatic ring. Such an addition has been evidenced in reactions of acyl halides with cyclo-olefins. Thus an intermediate chloroketone in the reaction of cyclohexene with acetyl chloride has been isolated [24]:



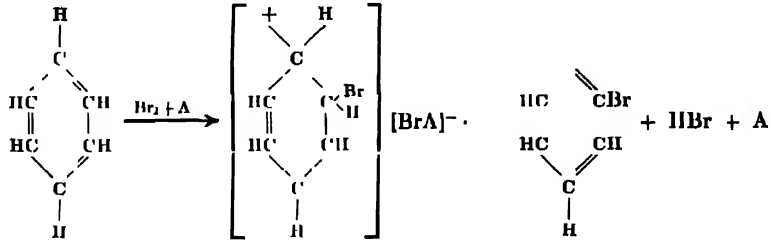
If reaction occurred similarly at an aromatic double bond, the first stage of an aromatic Friedel-Crafts reaction would consist of addition to the double bond of the ring which has become activated by a catalyst.

At present, the formation of a dihydrobenzene derivative as an intermediate in Friedel-Crafts reactions has been assumed by several investi-

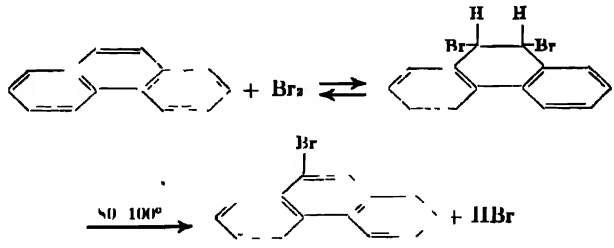
[24] H Wieland and L Bettag, *Ber.*, 55, 2246-2255 (1922).

gators [25] but it has not been definitely proved. However, investigations dealing with catalyzed bromination of aromatic hydrocarbons reveal formation of intermediate addition products in aromatic substitutions, and provide the basis for a theory which affords a logical interpretation of orientation and the effect of substituents in Friedel-Crafts reactions.

In a study of halogen-substitution as catalyzed by metal halides, Pfeiffer and Wizinger [26] advanced the formation of an intermediate carbonium ion in the bromination of benzene in the presence of halogen carrier (A):

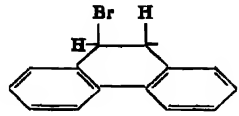


It has long been known that bromination of phenanthrene with bromine in carbon tetrachloride yields 9,10-dibromophenanthrene-9,10-dihydride, a crystalline product [27] which yields bromophenanthrene and hydrogen bromide upon heating at 80-100°. The dihydrodibromophenanthrene, commonly known as phenanthrene dibromide, has been a convenient source for the preparation of 9-bromophenanthrene.[28] The reaction of bromine with phenanthrene for the production of the monobrominated derivative obviously proceeds according to the scheme:

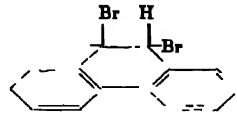


Price has measured the rate and equilibrium for the addition of bromine to phenanthrene,[29] the effect of substituents on the rate of bromination,[30] and the effect of catalysts on the phenanthrene-bromine reaction.[31] In the latter study he concluded that the reaction proceeded with intermediate formation of a free radical,

[25] W. Dilthey, *Ber.*, 71, 1350-1353 (1938), A. Schaarschmidt, *Z. angew Chem.*, 37, 286-288 (1924); *C A*, 18, 2874; see page 102, this book
[26] P. Pfeiffer and R. Wizinger, *Ann.*, 461, 132-154 (1928)
[27] M. Hayduck, *Ann.*, 167, 177-187 (1873). P C Austin, *J. Chem. Soc.*, 93, 1760-1767 (1908).
[28] W. E. Bachmann, *J. Am. Chem. Soc.*, 56, 1363-1367 (1934).
[29] C. Price, *J. Am. Chem. Soc.*, 58, 1834-1838 (1936).
[30] L. F. Fieser and C. Price, *J. Am. Chem. Soc.*, 58, 1838-1843 (1936).
[31] C. Price, *J. Am. Chem. Soc.*, 58, 2101-2104 (1936).

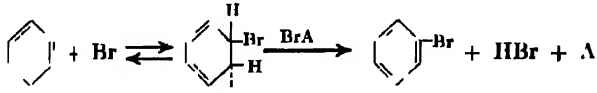


and subsequent formation of dihydrodibromophenanthrene,



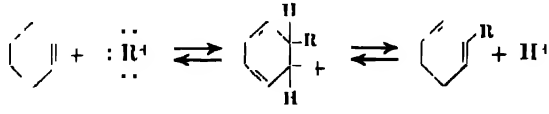
which is then dehydrohalogenated to monobromophenanthrene.

Kinetic studies indicated the intermediate formation of a free radical, rather than a carbonium ion as had been postulated by Pfeiffer and Wizinger.[26] Subsequently,[32] on the basis of Bruner's [33] measurements of the iodine-catalyzed bromination of benzene, it was determined that the kinetics of the iodine-catalyzed bromination of phenanthrene was identical with that of benzene. It was concluded that although the mechanism for the bromination of benzene could be expressed as



the kinetics of the reaction is incapable of distinguishing between the atomic and the ionic mechanisms, and that since iodine could conceivably effect the production of bromine ions instead of bromine atoms, the intermediate formed might have the structure which had been suggested by Pfeiffer and Wizinger.

On the basis of this work, Price [34] concludes that most aromatic substitutions proceed through an electron-deficient intermediate which acquires an electron pair from a double bond of the aromatic nucleus:



On the basis of this mechanism, orientation is governed by the electrostatic inductive effect of the substituent. A shift of the double bonds results, the shift being governed by the charge of the substituent. The following schemes are given for the negative (X) and positive (Y) substituents, respectively:

[32] C. C. Price and C. E. Arntzen, *J. Am. Chem. Soc.*, 60, 2835-2837 (1938).
[33] L. Bruner *Z. physik. Chem.*, 41, 513-543 (1902); *Bull. Acad. Sci. Cracow*, 181-200 (1902), *J. Chem. Soc. Abs.*, 82, 447 (1902).
[34] C. C. Price, "Aromatic substitution," Paper presented before Organic Division, American Chemical Society, Boston, 1939.

Assuming an alternate charge on every carbon atom, the substituent X induces shifting of the relative electron density to the *ortho* and *para* positions, whereas the substituent Y shifts the relative electron density to the *meta* position. Substituent Y, if sufficiently strong, may decrease the overall electron density of the aromatic nucleus to such an extent that further substitution is hindered or entirely inhibited.

Price points out that the "residual charge" of the atom may be calculated on the basis of the electron affinity of the atoms in their normal valence state, or from dipole moment data.[35] The following table, showing the relationship between orienting influence and residual charge, is of sufficient interest to warrant reproduction.

Orienting Influence and Residual Charge

Group	Residual Charge of Atom Attached to Ring — (Electron Affinity)	(Dipole Moment)	*Meta* Orientation
$-NH_2$	−1.6	−0.64	0
−OH	−1.2	0.44	3
OR	−1.2	−0.26	0
−Cl	−0.7	−0.21	0
−CH	0.0	−0.12	4
$-CH_2Cl$	0.7	0.13	4
$-NH_3^+$	1.3	0.07	47
COR	1.3	0.42	55
$-CHCl_2$	1.4	0.38	34
−COOH	1.9	0.55	82
−CN	1.9	0.63	80
−COCl	2.0	0.63	90
$-CCl_3$	2.1	0.63	64
$-NO_2$	2.4	1.36	93

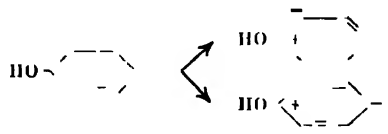
A similar relationship between dipole moments and orientation in aromatic substitution had been previously indicated by Svirbely and Warner.[36]

As the electron affinity and the dipole moment of the substituent increases, *meta* orientation is likewise increased. The overall electron density of the aromatic nucleus decreases as *meta* substitution becomes more pronounced, and reaction with positive ions is generally hindered; hence in the Friedel-Crafts reactions such substituents as COR, COOH, CN, and NO_2 are frequently referred to as deactivating groups. On the other hand, the groups NH_2, OH, OR, Cl, CH_3, and CH_2Cl, which are *ortho-para* directing groups, increase the overall electron density and

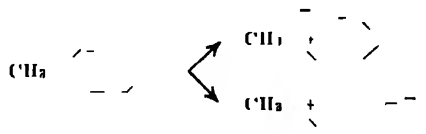
[35] R. S. Mulliken, *J. Chem. Phys.*, 2, 782 (1934).
[36] W. J. Svirbely and J. C. Warner, *J. Am. Chem. Soc.*, 57, 655-656 (1935).

thereby activate reaction with a positive charged ion. This does not mean, however, that all *ortho-para* directing groups facilitate Friedel-Crafts reactions. If the substituent, itself, has a replaceable atom, as in the case of the amino- group, Friedel-Crafts reaction, with substitution at carbon, is prevented; Friedel-Crafts reaction with phenols takes place only under certain conditions.

The effect of substituents on orientation can best be explained electromerically.[37] Activation, with production of a negative carbon atom, may be effected by a substituent group. This is illustrated in the case of phenol:

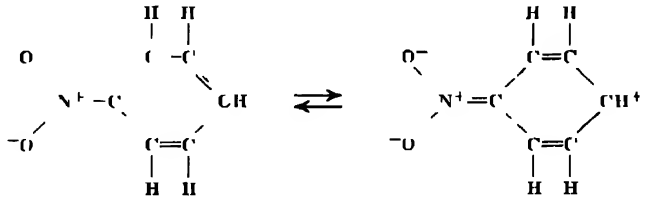


This occurs to a lesser extent with toluene; here the methyl group is attached to the benzene ring at the negative end of a dipole:



Conditions are thereby effected for the formation of *ortho-* and *para-* derivatives by reaction of negative carbon with an available cation.

When the substituent is present in the benzene ring at the positive end of the dipole, electromeric change may occur as it does with nitrobenzene:

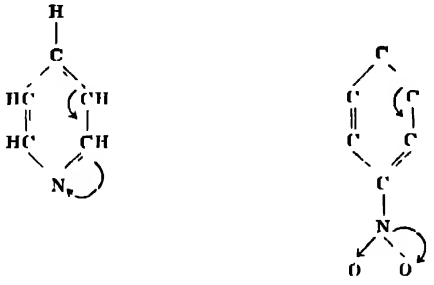


The drift of electrons prevents reaction with cations in the *para* and *ortho* positions; substitution, if it occurs, is in the *meta* position. The nitro- group, however, effects such a strong electropositive field, that it tends to hinder entrance of a cation even at the *meta* position. Nitrobenzene, therefore, does not undergo Friedel-Crafts reactions. The deactivating effect of the nitro- group has been found to extend even to the remote ring of such a compound as nitrobiphenyl. In nitration, the unsubstituted phenyl group is clearly deactivated by the nitro- group situated at the extreme end of the other nucleus. Dipole moments of

[37] See W. A. Waters and T. M. Lowry, "Physical Aspects of Organic Chemistry," pp. 425-452, 1937.

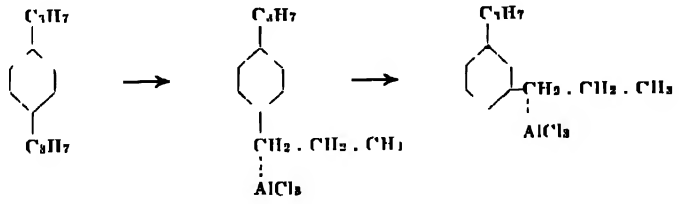
nitrobenzene and *p*-nitrobiphenyl have been found to be of approximately the same order.[38]

The electronic disturbances in nitrobenzene are similar to those possible in pyridine. Sidgwick [39] indicates these as follows:

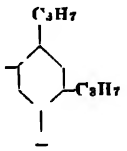


Pyridine, like nitrobenzene, thus does not undergo Friedel-Crafts reaction with alkyl or acyl halides.

Meta-orientation in Friedel-Crafts reactions with toluene has been occasionally reported, especially by earlier investigators *; and it has been recently shown [40] that *meta*-substitution is due to primary formation of *para*-derivatives and subsequent conversion into the *meta*-derivative. The change of *p*-dipropylbenzene to *m*-dipropylbenzene was assumed to proceed by migration of a complex of aluminum chloride with the propyl group:



The stability of the *meta*-derivative may be explained by assuming anionoid centers *para* to the alkyl groups.



Upon contact with aluminum chloride, therefore, only the unsubstituted positions 4 and 6 are affected. Baddeley and Kenner reported no isomer-

[38] C. G. LeFevre and R. J. W. LeFevre, *J. Chem. Soc.*, 1130-1137 (1936).
N. V. Sidgwick, "The Organic Chemistry of Nitrogen," p. 523, 1937.
* See pages 82 and 87.
[40] G. Baddley and J. Kenner, *J. Chem. Soc.*, 303-309 (1935).

ization during migration of the *n*-propyl group. This has been questioned by Nightingale.[41]

Since rearrangement of dialkyl benzenes to *m*-derivatives takes place at higher temperatures in the presence of aluminum chloride, it has been concluded [42] that *m*-substitution in Friedel-Crafts reactions is a function of temperature.

Effect of Heat. Nenitzescu and his co-workers [23] have shown that with reactive components, Friedel-Crafts reactions may be effected in the *absence* of a catalyst. When benzyl chloride was heated with such highly aromatic compounds as biphenyl, naphthalene, anisole, and mesitylene, the expected diarylmethane derivatives were secured. Similarly, benzoyl chloride acylated biphenyl, naphthalene or anthracene simply by heating the reactants in the presence of nitrobenzene. An almost quantitative yield of 9-benzoylanthracene was secured in this way. Since these condensations proceed in analogous manner but at lower temperature in the presence of aluminum chloride, the Friedel-Crafts reaction may not necessarily involve formation of a complex with a metal halide catalyst. The fact that certain reactions can be effected either by thermal excitation or by aluminum chloride indicates only that aluminum chloride, like heat, is capable of activating the reactants involved, and it does not explain the mechanism through which the activation is brought about; however, the possibility that both heat catalysis and metal halide catalysis may follow the same path should be borne in mind.

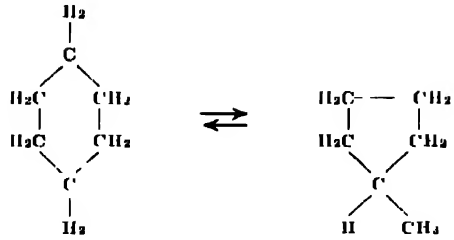
Aliphatic Reactions

Instances citing the "loosening" effect of aluminum chloride as evidenced in a number of aliphatic reactions effected in the presence of this catalyst have been pointed out by Nenitzescu [43] who expresses the following views:

a) Halogen ions or halogen compounds which easily ionize, form stable molecular compounds with aluminum chloride.

b) In saturated hydrocarbons the electrons are bound so fast to the carbon atoms that the formation of a stable molecular compound cannot be considered. The action of aluminum chloride on saturated hydrocarbons can be explained only by the fact that the aluminum chloride causes an *attraction* of the electrons of carbon atoms, whereby a reversible *deformation of the electron shells* of these carbon atoms occurs. The consequence of this deformation is a loosening of one or more bonds so that isomerization of the carbon chain is made possible, as for example [44]:

[41] D. V. Nightingale, *Chem Reviews*, **25**, 354 (1939).
[42] J. F. Norris and D. Rubinstein, *J. Am. Chem. Soc.*, **61**, 1163-1170 (1939).
[43] C. D. Nenitzescu, D. A. Isacescu, and C. N. Ionescu, *Ann.*, **491**, 210-220 (1931); *C. A.*, **26**, 1257.
[44] C. D. Nenitzescu, *Personal communication.*
[44] C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, **66**, 1097-1100 (1933).



Aliphatic hydrocarbons likewise undergo isomerization.

c) If acceptors for hydrogen are present, the hydrogen is given off, and there results a true, stable, molecular compound of aluminum chloride and the resulting olefin. This compound of aluminum chloride with an olefin is identical with that to be described under (d); and it is in most cases very unstable so that it is again changed immediately.

Halogen compounds, both organic [45] and inorganic,[46] have been shown to act as acceptors for the hydrogen evolved. Further, the saturated carbon chains themselves can also act as acceptors for the hydrogen, by breakdown to lower molecular weights.

The hydrogen in the saturated hydrocarbons is strongly activated, for which reason it is capable of all possible reductions of halogen compounds. A beautiful example of this is the formation of the hydrocarbon $C_{12}H_{22}$ from cyclohexane, C_6H_{12}. (See under (d).)

This reaction proceeds at 0°C with great velocity if an acceptor for the hydrogen is present (Reaction (b).) This explains why cyclohexane can be heated with aluminum chloride *alone* for a long period at 80° without decomposing the molecule.[47]

Ipatieff and Komarewsky [48] have shown that if the temperature is increased to 150°, cyclohexane gives the hydrocarbon $C_{12}H_{22}$ and lower hydrocarbons, especially isobutane.

The following explanation is the only one possible for the reaction occurring at 150°: The hydrogen which is freed by the formation of the hydrocarbon $C_{12}H_{22}$ uses as acceptor the carbon chain of the cyclohexane molecule itself, which changes into the observed lower hydrocarbons. The carbon chain C—C is even a poorer acceptor for hydrogen than the carbon-halogen bond, R—X. For this reason the reaction, in the absence of halogen compounds as acceptors, requires a much higher temperature.

If aluminum chloride is allowed to react on *n*-hexane at boiling temperature,[49] only a very small amount of lower hydrocarbons is formed, and there is only a very small amount of (polymerized) olefins in the "lower layer."

[45] C. D. Nenitzescu and C. N. Ionescu, *Ann.*, **491**, 189-210 (1931); C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, **65**, 807 812, 1449-1453 (1932).
[46] C. D. Nenitzescu and D. A. Isacescu, *Ber.*, **67**, 1391-1393 (1934).
[47] C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, **66**, 1097-1100 (1933).
[48] V. N. Ipatieff and V. I. Komarewsky, *J. Am. Chem. Soc.*, **56**, 1926-1928 (1934).
[49] C. D. Nenitzescu and A. Dragan, *Ber.*, **66**, 1892-1900 (1933).

Most of the unchanged *n*-hexane is directly isomerized and cyclized without previously undergoing a cleavage. If cleavage and later addition of olefin to paraffin had taken place, more side-products would have been formed. These same views apply also to the above-mentioned isomerization of cyclohexane into methylcyclopentane[47] which occurs at 80°, with practically no development of gaseous hydrocarbons, and without the formation of olefins in the lower layer.

d) Olefins have an extraordinarily great affinity for aluminum chloride. If, for example, a dilute solution of an olefin in an inert solvent like carbon disulfide is shaken with aluminum chloride, the entire olefin is immediately precipitated on the aluminum chloride, and the resulting layer of carbon disulfide is free of olefins. This reaction is quantitative.

The complex which results contains a carbon atom which has only 6 electrons and which is therefore unstable. Only seldom can the olefin be recovered from this complex. The following may occur:

(1) A rearrangement of the carbon skeleton.
(2) An addition of hydrogen chloride.
(3) An addition of acid chloride, $RCOCl.AlCl_3$, activated by aluminum chloride (see below under (f)).
(4) A polymerization.

In the last case the Whitmore conception applies fully.[50] Polymerization is the rule when no addendum, as HX or RCOCl is present. For example, if the lower layer in the preceding experiment is decomposed with water, polymeric olefins are obtained for the greater part.

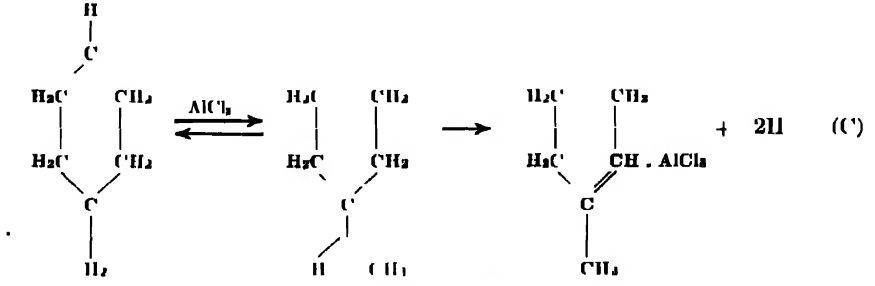
The mechanism of dehydrogenation during polymerization is still not clear. Such a dehydrogenation is seen in the formation of the hydrocarbon $C_{12}H_{22}$, as given below.[45]

$$2C_6H_{12} \longrightarrow C_{12}H_{22} + 2H \qquad (A)$$

Here the hydrogen can be taken up by all possible acceptors, as for example:

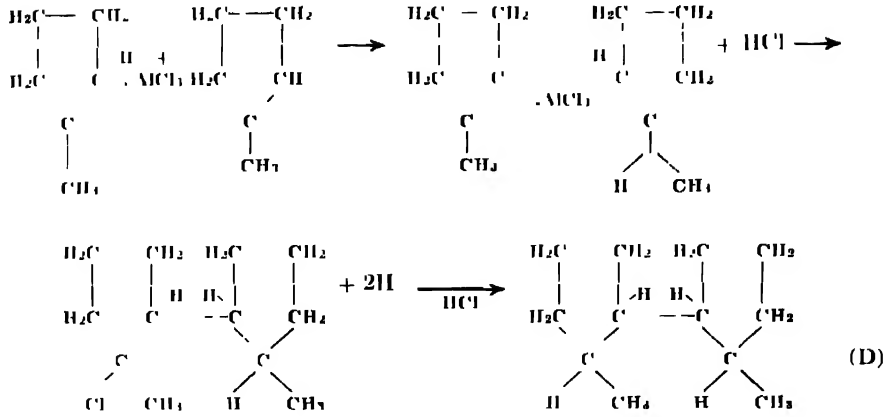
$$2H + RCl \longrightarrow HCl + R.H \qquad (B)$$

This appears to occur probably according to the following scheme:



(C)

[50] F. C. Whitmore, *J. Am. Chem. Soc.*, **54**, 3274-3283 (1932).



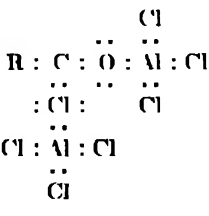
(D)

A proof of this opinion lies in the fact that the reaction can be held in the first phase (C) by weak, poisoned catalysts. In this phase the olefin is stabilized by the addition of CH_3COCl.[51] Here no hydrocarbon $C_{12}H_{22}$ is formed, since the weakened catalyst cannot bring about the irreversible hydrogenation of step (D).

e) The aromatic hydrocarbons are in a middle position between the saturated hydrocarbons and the olefins, that is, they form no stable compounds, as do olefins, but their electron shells are considerably more deformed than those of saturated hydrocarbons, so that they are capable of the known reactions.

f) Halogen atoms in the simple halogen compounds are deformed (activated) without being able to form molecular compounds. This is known by the fact that halogen migration in carbon chains can occur,[52] and is further evidenced in Friedel-Crafts condensations.

Acid chlorides form stable compounds which possibly are dissociated: $(RCO)^+(AlCl_4)^-$. These complexes react only slowly with aromatic hydrocarbons. If a small excess of aluminum chloride, over that amount which corresponds to a molecule, is added, there results a compound:



which reacts considerably more quickly (since it contains a carbon atom with an incomplete octet). This fact was first observed by Olivier,[53]

[51] C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, 65, 1449-1453 (1932).
[52] C. D. Nenitzescu and I. G. Gavat, *Ann.*, 519, 260-271 (1935); C. D. Nenitzescu and D. Curcanenu, *Ber.*, 70, 846-848 (1937).
[53] S. C. J. Olivier, *Rec. trav. chim.*, 33, 91-182 (1914); *C. A.*, 8, 3013.

who pointed out by reaction velocity measurements the greater catalytic activity of the aluminum chloride in excess.

The action of aluminum chloride in isomerization, dehydrogenation, cracking, polymerization, and Friedel-Crafts reactions in the aliphatic and cycloaliphatic series is thus briefly summarized by Nenitzescu:

(1) Under the action of aluminum chloride the saturated hydrocarbons undergo an isomerization of the carbon chain which leads to an equilibrium. This isomerization is an immediate reaction, comparable with keto-enol tautomerism and is not limited by cleavage and further addition.

(2) Under some extreme conditions (at high temperatures) the hydrogen atom is cracked off from the carbon atom. This is immediately taken up by another molecule, which by scissure at C—C bonds decomposes into lower saturated hydrocarbons This reaction is the basis for the cracking of hydrocarbons with aluminum chloride (McAfee process, etc). If hydrogen acceptors are added, the cleavage of hydrogen occurs at 150° and lower temperatures.

(3) The branched hydrocarbons crack off the hydrogen atom and change into olefins considerably more easily than the unbranched hydrocarbons It is for this reason that in the action of aluminum chloride and an acyl halide on cyclohexane, isomerization occurs, with the formation of methylcyclopentane, and there is obtained a ketone *only* with the cyclopentane ring

(4) The olefins, which are formed from paraffins as has been shown above under (2), polymerize, and remain bound fast with the aluminum chloride. A part of this polymer can add hydrogen chloride and then be reduced by the active hydrogen atom There are thus formed higher saturated hydrocarbons (as that of the type to which the compound $C_{12}H_{22}$ belongs) which leave the lower layer and go into the upper. Naturally these compounds, like the original hydrocarbons, can be isomerized, dehydrogenated, cracked, and polymerized, for which reason the picture of the reaction is complicated.

(5) The addition of olefins to paraffins under the influence of aluminum chloride is thus understood: The paraffin is first dehydrogenated. The resulting olefin polymerizes with the already present olefin, and is changed into a dimer, which is then hydrogenated to a saturated hydrocarbon according to the scheme given above. The hydrogen necessary for this reaction comes from the dehydrogenation of the paraffin. As an intermediate phase of the polymerization can be assumed an addition of hydrogen chloride as noted in (d) (D).

Our Proposed Proton Theory.—Many reactions catalyzed by aluminum chloride require the use of hydrogen chloride as an activating agent. This has been repeatedly noted in reactions which involve addition to an olefinic double bond, as for example, in the alkylation of benzene with olefins. Early investigators assumed that in reactions of this type hydrogen chloride was needed to convert the olefin into an alkyl halide. Such an assumption, of course, entails its corollary: that alkylation with

olefins, and hence all reactions effected with olefins in the presence of aluminum chloride, proceeds by the primary formation of an alkyl halide. The question of olefins versus alkyl halides as the active agents in Friedel-Crafts reactions is still debatable, for evidence has been offered * partially to substantiate the assumption that alkylation with alkyl halides occurs through conversion of the alkyl halide into an olefin.

This distinct contradiction does not help in accounting for the known activating effect of hydrogen chloride. Moreover, it has been noted in many instances that even in condensations effected with alkyl halides or other chlorinated compounds, the presence of traces of moisture in the aluminum chloride has an accelerating effect. It has been shown, too, that cracking of paraffinic hydrocarbons does not take place in the presence of aluminum chloride which had been freed of hydrogen chloride by melting under pressure with powdered aluminum.[21] From this we may infer that hydrogen chloride, either present as such or produced by reaction of water with the catalyst, has an activating influence not only on reactions involving olefins, but also on condensation with alkyl halides and on cracking. However, the importance of hydrogen chloride for Friedel-Crafts reactions in general can be determined only by working with absolutely anhydrous aluminum chloride; and, since the compound takes up moisture avidly, it is questionable whether anyone has ever been able to prepare aluminum chloride in a totally anhydrous state. In this laboratory we have made repeated attempts to prepare thoroughly anhydrous aluminum chloride without success. Contamination by moisture from this source is, therefore, difficult to avoid. Although aluminum chloride reactions are commonly regarded as taking place under anhydrous conditions, it is questionable whether the reactants themselves are ever entirely moisture-free. Benzene, for example, is rendered anhydrous only with difficulty; in the majority of procedures involving this hydrocarbon no attempt is made to remove the last traces of moisture from it. The apparatus used may be another source of contamination. The technical difficulties involved in attempting the total exclusion of water from Friedel-Crafts reactions lead us to believe that traces of moisture, and hence of hydrogen chloride, are unavoidably present. It is thus possible that all the reactions which are generally attributed to catalytic activity of anhydrous aluminum chloride are really caused by a combination of aluminum chloride with hydrogen chloride. Aluminum chloride containing neither moisture nor hydrogen chloride may be found to be entirely useless for catalyzing Friedel-Crafts reactions.

If hydrogen chloride is conceded to be generally beneficial in aluminum chloride catalysis, any explanation of its activity should be applicable to all the reactions promoted by this catalyst.

Although aluminum chloride absorbs gaseous hydrogen chloride until a definite point of saturation has been reached, and although the author has found that aluminum chloride which has been treated in this way is

* See pages 33 and 103.

[21] V. N. Ipatieff and A. V. Grosse, *Ind. Eng. Chem.*, 28, 461-464 (1936).

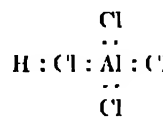
a more active agent than ordinary anhydrous aluminum chloride, nothing is known about the manner in which hydrogen chloride combines with aluminum chloride. It is known, however, that aluminum chloride forms addition compounds with ammonia, sulfur chloride, hydrogen sulfide, hydrogen cyanide, and phosphine. It forms definite compounds with many metallic halides, yielding the very useful catalyst, $NaAlCl_4$, with sodium chloride. Hydrogen chloride would be expected to form an analogous compound,

$$HCl + AlCl_3 \longrightarrow HAlCl_4$$

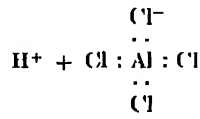
but such a compound has not been isolated.

Boron trifluoride, which resembles aluminum chloride in catalytic activity, does give isolable compounds with a number of acids. Its complex with boric acid, dihydroxyfluoroboric acid, has been shown to be an extremely effective catalyst for certain polymerizations, and it forms analogous compounds with acetic and formic acid

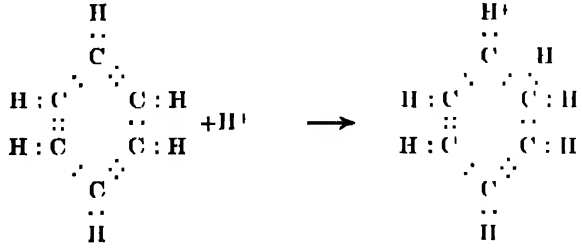
A complex of aluminum chloride with such an acid as hydrogen chloride would, by analogy, be expected to have unusual catalytic properties. It should have the electronic structure,



and on this basis should be a highly ionizable acid.*



The author's explanation of the activating effect of hydrogen chloride is based on the formation of the very reactive proton as postulated above, the activation proceeding as it has been shown to proceed in acid-catalyzed polymerizations and isomerizations. The effect of the hydrogen ion on benzene can be formulated as follows:



* In this connection it is interesting to note that the conductivity of an anhydrous toluene solution of aluminum bromide is increased over 1000 times upon addition of hydrogen bromide. See J. F. Norris and J. E. Wood, *J. Am. Chem. Soc.*, 62, 1428-1432 (1940).

The resulting hydrogenated benzene, set into a very unstable state, would thus be sufficiently activated to permit ready substitution. Any compound having an unshared pair of electrons, for example an olefin, would add with the proton in analogous manner. The addition of the proton to an alkyl halide at the halogen, followed by shifting to a more stable state, would likewise account for isomerization of this type of reactant, and for accompanying activation. It is thus possible that in some Friedel-Crafts reactions both the aromatic and aliphatic component are activated. In its attempt to secure electrons, the proton can be expected to have a disrupting effect on saturated aliphatic hydrocarbons, evidenced by cracking and isomerization.

The formation of the active intermediate, $HAlCl_4$, and its ready ionization into H^+ and $AlCl_4^-$ thus can account for the manifold reactions catalyzed by aluminum chloride. Here, too, we have a coördination of aluminum chloride catalysis with acid-catalyzed reactions, as well as an explanation of the similarity in reactivity of other metal halide catalysts which are capable of forming an addition compound with hydrogen chloride. Unlike the "complex theory," our theory is not hampered by necessary correlation of complex formation with activity, which too often can be done only inadequately. Neither must we contend with the disturbing fact that many of the known aluminum chloride complexes are, after all, too stable to promote reaction.

This thought has been partially brought out by Ipatieff and his coworkers,[22] who have suggested that the role of hydrogen chloride in some reactions may be explained by assuming that the compound, $HAlCl_4$, itself form addition products with the reactants. Thus it has been postulated that olefins react with $HAlCl_4$ to yield esters which are analogous to those obtained with sulfuric acid, and that the esters thus formed react with aromatic hydrocarbons to yield alkylated products:

$$RCH:CH_2 + HAlCl_4 \longrightarrow \underset{\displaystyle ClAlCl_3}{RCH.CH_3} \xrightarrow{C_6H_6} C_6H_5\underset{\displaystyle R}{\overset{\displaystyle CH_3}{CH}}$$

The alkylation of aromatic hydrocarbons with alcohols is similarly assumed to proceed by the formation of an addition compound of $HAlCl_4$ with the alcohol. These assumptions were advanced to show that, since reaction does not result in the production of branched alkyl benzenes, in the instances studied it could not proceed through intermediate formation of alkyl halides. However, Ipatieff's explanation falls down in that it does not account for reactions of substances which cannot be esterified. If the compound, $HAlCl_4$, does add to Friedel-Crafts reactants in general, it could do so in many instances only by hydrogen bonding. Although such a possibility suggests interesting speculation, if hydrogen bonding did occur, the resulting complex probably would ionize to give

[22] V. N Ipatieff, H. Pines, and L. Schmerling, *J. Org. Chem.*, 5, 253-263 (1940).

the same product which would be obtained by direct addition of a proton In aluminum chloride catalysis we have to deal not only with compounds which react with even very highly ionized acids, but with comparatively inert paraffins, with compounds like acid halides and anhydrides which are highly acidic in themselves, and with difficultly disrupted aromatic nuclei

The proton theory which we are advancing does explain the mechanism through which the catalyst is able to effect such a miscellany of reactions as cracking of paraffins or of aromatics, dehydrogenating condensations of aromatic nuclei, isomerizations and rearrangements in both the aliphatic and aromatic series, polymerization, and alkylation We believe that the highly activated proton can effect an unbalancing of molecules which leads to reactions of this wide range

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Chapter 5

Friedel-Crafts Syntheses Part 1

The use of aluminum chloride as a catalyst for reactions involving evolution of hydrogen chloride embraces a wide field of organic chemistry. The reaction proceeds according to the general scheme:

$$RH + R'X \longrightarrow RR' + HX$$

With a few exceptions R may be any cyclic compound, substituted or unsubstituted, and R'X may be any halogenated compound. The ease of reactivity is in accordance with rules governing aromatic substitution, the presence of activating groups in the aromatic component facilitating reaction. Increasing negativity of the compound which is to be substituted hinders reaction. Thus most polyhalogenated derivatives, nitrocompounds, and heterocyclic compounds of nitrogen are substituted with difficulty. Recently the reaction has been extended to substitution of aliphatic and cycloaliphatic compounds. The effect of substituents in the halogenated component, although not so marked, also limits the scope of the reaction. Whereas the reaction has been most generally applied to condensations effected with alkyl or acyl halides, many halogenated esters, acids, lactones, ketones, ethers, aldehydes, nitrogenous compounds, and inorganic halides also undergo the reaction with replacement of halogen.

Although within recent years the term "Friedel-Crafts reaction" has been construed to mean any condensation or addition in which anhydrous aluminum chloride or other metallic halide is used as catalyst, it was originally used to denote only those reactions in which a hydrogen halide was given off during the course of the reaction. Unless one adheres to this older conception of the reaction, it is difficult to correlate the various organic reactions in which aluminum chloride is used as a catalyst. Not all such reactions are subject to the same limitations; operations in which, for example, water is split off, are necessarily performed under conditions which are very different from those in which a hydrogen halide is formed.

Due to the great extent of work which has been done on Friedel-Crafts syntheses with acyl halides, reactions of this type have been included in a separate chapter.* Friedel-Crafts syntheses in which both reactants are aliphatic have likewise been given separate treatment.†

* See Chapter 6. For ring closures with evolution of HX see Chapter 7.

† See Chapter 17.

Reaction of Benzene or Benzene Homologs with Unsubstituted, Saturated Alkyl Halides

The following rather detailed account of the reaction of *n*-amyl chloride with benzene is given in order to illustrate the factors which must be observed for controlling a Friedel-Crafts alkylation. Owing to isomerization by aluminum chloride, a mixture of isomers is obtained.

A two-liter three-neck flask is provided with a mercury seal—or other seal—stirrer, dropping funnel, reflux condenser, and thermometer. Four hundred and twenty-nine grams of benzene (5.5 moles), dried over calcium chloride, are placed in the flask, then 15 g of powdered anhydrous aluminum chloride (.113 mole) is added. With stirring, 106.6 g of *n*-amyl chloride (1 mole) is added dropwise for a period of one and a half hours from the funnel, which is protected with a calcium chloride drying tube. Another drying tube is placed at the top of the reflux condenser. A tube may be inserted at this point to lead the liberated hydrogen chloride to a

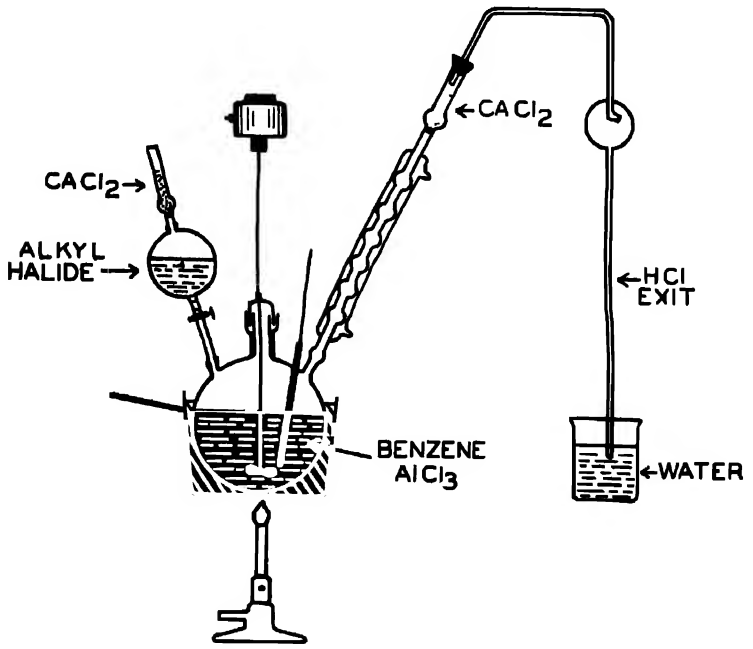

Fig. 4. Apparatus for Friedel-Crafts Alkylation.

hood; or the gas may be trapped in water by dipping the outlet tube slightly below the surface of about 300 cc of water contained in a beaker. In order to make an accurate material balance, the hydrogen chloride should be scrubbed.

The addition of *n*-amyl chloride takes place over a period of one and a half hours, and at this rate the temperature should rise only slightly above 20°C. To complete the reaction, the mixture may be stirred for

an additional period of six hours at 20°C, or two hours at a slightly elevated temperature, *e.g.*, 50°C.

When the reaction is complete, the stirring is stopped and the mixture is allowed to stand for about two hours. The catalyst complex settles to the bottom during this time. The upper layer is then removed by means of a siphon, or by decantation, and treated with approximately 5 cc of 30 per cent sodium hydroxide, shaking vigorously. When the mixture tests neutral or alkaline to litmus, it is filtered, and fractionated. There should be only a small quantity of water present at this stage.

The unreacted benzene is removed by distillation at atmospheric pressure. A Vigreaux-type column about 24" long is suitable. To obtain the desired product, the residue, after benzene removal, is distilled and the fraction boiling at 185-205°C is collected.

The first point brought out here is that all reactants must be dry and that provision is made for the exclusion of moisture. This precaution is necessary for all reactions involving the use of anhydrous aluminum chloride.

In order to increase the yield of the desired product, the amount of aluminum chloride to be used for the reaction must be carefully determined. In order to prevent polyalkylation of the benzene an excess of the latter is used.

It has been found that stirring aids the reaction. In the laboratory effective stirring may be secured at 1500 r.p.m. with a one-inch blade. This is started before the first portion of the *n*-amyl chloride is added. The addition of the halide is gradual.

Since the Friedel-Crafts alkylation is reversible,

$$HX + RR' \qquad RH + R'X$$

it is necessary that the hydrogen chloride be removed from the reaction mixture as soon as it is evolved. This is provided for by an outlet tube through which the liberated gas escapes. When no more hydrogen chloride is given off, the alkylation is known to be complete, provided moisture or other impurities has not decreased the activity of the catalyst.

At this point, the reaction mixture contains essentially alkylated benzenes, the unreacted benzene, and the catalyst complex. The upper layer is removed to decrease the color of the final product and also to simplify the fractionation. A small quantity of the product is lost in the complex. After washing, amylbenzene is separated by distillation from the unreacted benzene and the lower alkylated benzenes (present in small quantities) and the high-boiling polyalkylated benzenes. There were obtained 112 g of a mixture of isomeric amylbenzenes, b. 120-145°/100 mm, and 12.5 g of a residue, n_D^{20} 1.5250. Refractionation gave 105 g of a product boiling at 185-205°, n_D^{20} 1.4892, or a 71 per cent theoretical yield.

The factors governing this reaction, as all Friedel-Crafts reactions, may be summarized thus:

1. Concentration of reacting components.
2. Concentration of catalyst.
3. Solvent or diluent used.
4. Exclusion of moisture.
5. Elimination of hydrogen halide.
6. Temperature (and sometimes pressure).
7. Reaction time.
8. Manner of introduction of reactants.
9. Agitation.
10. Removal of desired product from by-products and unreacted material.

It is obviously impossible to list as thoroughly as has been done in the case of the preparation of amylbenzene the influence of each of these conditions on the course of every Friedel-Crafts alkylation. Nevertheless in the discussion of specific reactions which follows, definitely necessary governing factors will be indicated. Even a cursory review of the Friedel-Crafts preparation of many substances will enable a determination of conditions which should be observed in the synthesis of the various types of compounds.

A number of alkylbenzenes prepared by the interaction of benzene with an alkyl halide in the presence of aluminum chloride are listed in Table 3. In Tables 4 and 5 are listed some aluminum chloride-catalyzed reactions of alkylbenzenes with alkyl halides.

Inspection of these tables indicates that generally alkyl halides with benzene yield *meta*- and *para*-compounds in di-substitution. Monoalkyl benzenes, for example, toluene, also generally give *meta*- and *para*-compounds upon introduction of one alkyl group. *m*-Xylene with alkyl halides gives the symmetrical derivatives almost exclusively:

Here again the methyl groups appear to have a *meta*-directing force.

In other Friedel-Crafts reactions, however, *ortho*- and *para*-substitution is the rule. A number of investigators have attempted to show that no exception to the rule occurs in Friedel-Crafts alkylations, but that the formation of *meta*-derivatives is here due to rearrangement of primarily formed *para*-derivatives.

Reaction of toluene with various butyl halides illustrates orientation of the entering group in Friedel-Crafts alkylation of mono-alkylated benzenes. Alkylation of toluene with isobutyl bromide has been stated to give a mixture of *m*- and *p*-isobutyltoluenes,[47] only *m-tert*-butyltoluene,[48] and a mixture of *m*- and *p-tert*-butyltoluenes.[49] The reaction of *tert*-

(Text cont'd on p. 84)

[47] W. Kelbe and G. Pfeiffer, *Ber.*, 19, 1723-1730 (1886).
[48] A. Baur, *Ber.*, 24, 2832-2843 (1891).
[49] J. B. Shoesmith and J. F. McGeehen, *J. Chem. Soc.*, 2231-2236 (1930); *Brit. Chem. Abstracts-A*, 79 (1931).

. Table 3.—Alkylation of Benzene

Compound Formed	Alkyl Halide	Prepared by
Toluene	methyl chloride	1, 21
m-Xylene	methyl chloride	1, 156
p-Xylene	methyl chloride	1, 156
1,3,5-Trimethylbenzene	methyl chloride	21, 100, 154
1,2,4-Trimethylbenzene	methyl chloride	21, 100, 154
1,2,4-Trimethylbenzene	methyl bromide	205
1,2,4,5-Tetramethylbenzene	methyl chloride	2, 21, 100, 154
Pentamethylbenzene	methyl chloride	1, 21, 100, 154
Hexamethylbenzene	methyl chloride	21, 100, 154
Ethylbenzene	ethyl halide	1, 8, 7, 11, 21, 167, 174, 175, 176, 177
m-Diethylbenzene	ethyl halide	3, 172, 178
p-Diethylbenzene	ethyl halide	3, 172-3, 178
1,2,4-Triethylbenzene	ethyl chloride	179, 209
1,3,5-Triethylbenzene	ethyl chloride	179, 198, 209
1,3,5-Triethylbenzene	ethyl bromide	205
1,2,3,4-Tetraethylbenzene	ethyl bromide	4, 180
1,2,4,5-Tetraethylbenzene	ethyl halide	4, 180, 209
1,2,3,5-Tetraethylbenzene	ethyl chloride	209
Pentaethylbenzene	ethyl bromide	5, 181
Hexaethylbenzene	ethyl chloride	7, 182
Hexaethylbenzene	ethyl bromide	183
Propylbenzene	propyl chloride	184, 30
Propylbenzene	propyl bromide	15, 185, 186
Isopropylbenzene	propyl chloride	184, 30
Isopropylbenzene	propyl bromide	15
Isopropylbenzene	isopropyl bromide	163, 181
Isopropylbenzene	isopropyl chloride	17
m-Di-isopropylbenzene	isopropyl chloride	17, 171
o-Di-isopropylbenzene	isopropyl chloride	17, 171
1,3,5-Tri-isopropylbenzene	isopropyl chloride	191
Tetra-isopropylbenzene	isopropyl chloride	7, 16
m-Dipropylbenzene	propyl bromide	186
p-Dipropylbenzene	propyl bromide	186
Hexapropylbenzene	propyl chloride	7
sec-Butylbenzene	*n*-butyl chloride	19, 188
tert-Butylbenzene	*n*-butyl fluoride	199
tert-Butylbenzene	isobutyl bromide	188
tert-Butylbenzene	*tert*-butyl chloride	21, 188, 190
n-Butylbenzene	butyl chloride	16, 19
Di-isobutylbenzene	butyl chloride	16
Tri-isobutylbenzene	butyl chloride	16
p-Di-*tert*-butylbenzene	isobutyl chloride	190
Tri-*tert*-butylbenzene	isobutyl chloride	190
2-Methyl-3-phenylbutane		
tert-Amylbenzene	isoamyl chloride	189, 192
Isoamylbenzene		
tert-Amylbenzene	*tert*-amyl bromide	187
Amylbenzenes	amyl chloride	1, 21
?-Amylbenzene	isoamyl chloride	188
Diamylbenzene	"active" amyl chloride	201
2-Methyl-3-phenylbutane	neopentyl chloride	210
Octadecylbenzene	octadecyl bromide	202, 203

Table 1. Alkylation of Toluene

Compound Formed	Alkyl Halide	Prepared by
m-Xylene	methyl chloride	1, 151, 156, 195, 205
p-Xylene	methyl chloride	1, 151, 156, 195
o-Xylene	methyl chloride	151, 205
1,2,4-Trimethylbenzene	methyl chloride	1, 100, 151, 156
1,3,4-Trimethylbenzene	methyl chloride	195
1,3,5-Trimethylbenzene	methyl chloride	1, 100-1, 151, 156, 195
1,3,4,6-Tetramethylbenzene	methyl chloride	195
1,2,4,5-Tetramethylbenzene	methyl chloride	1, 100, 151-2, 156
1,3,4,5-Tetramethylbenzene	methyl chloride	195
1,2,3,5-Tetramethylbenzene	methyl chloride	151, 156
Pentamethylbenzene	methyl chloride	1, 100, 151, 154, 195
Hexamethylbenzene	methyl chloride	1, 100, 151, 154, 195
1-Methyl-3-isopropylbenzene	isopropyl bromide	167
1-Methyl-3-isopropylbenzene	isopropyl iodide	207
?-Isopropyltoluene	isopropyl chloride	171
?-Isopropyltoluene	*n*-propyl chloride	171
m-*sec*-Butyltoluene	*n*-butyl chloride	168
p-*sec*-Butyltoluene	*n*-butyl chloride	168
m-*tert*-Butyltoluene	*tert*-butyl chloride	158, 168
p-*tert*-Butyltoluene	*tert*-butyl chloride	168
m-*tert*-Butyltoluene	isobutyl bromide	168, 196 197
m-*tert*-Butyltoluene	isobutyl chloride	157, 158
p-*tert*-Butyltoluene	isobutyl bromide	168, 197
p-*tert*-Butyltoluene	isobutyl chloride	157
m-*tert*-Butyltoluene	isobutyl iodide	158, 159
1,3-Dimethyl-5-*tert*-butylbenzene	isobutyl bromide	159
1,4,-Di-*tert*-butylbenzene	isobutyl bromide	159
x,*x*-Di-*tert*-butyltoluene	isobutyl bromide	159
1-Methyl-3-*tert*-amylbenzene	*tert*-amyl chloride	164, 165

Table 5—Alkylation of Alkylated Benzenes other than Toluene

Aromatic Hydrocarbon Used	Alkyl Halide Used	Compound Formed	Prepared by
Ethylbenzene	isopropyl or propyl bromide	*m*-ethylisopropylbenzene	162
Ethylbenzene	isopropyl or propyl bromide	*p*-ethylisopropylbenzene	162
Propylbenzene	isopropyl bromide	*p*-propylisopropylbenzene	186
Propylbenzene	isopropyl bromide	*m*-propylisopropylbenzene	186
Isopropylbenzene	isobutyl chloride	*tert*-butylbenzene *p*-di-*tert*-butylbenzene propyl chloride	200
Xylene	methyl chloride	trimethylbenzenes	211
Xylene	methyl chloride	durene	153, 206
Xylene	methyl chloride	pentamethylbenzene	153, 206, 211
Xylene	methyl chloride	hexamethylbenzene	153
m-Xylene	methyl chloride	pseudocumene	151
m-Xylene	methyl chloride	1,3,5-trimethylbenzene	151, 205
m-Xylene	ethyl bromide	1,3-dimethyl-5-ethylbenzene	194
m-Xylene	ethyl bromide	1,5-dimethyl-2-ethylbenzene	194
m-Xylene	*n*-propyl or isopropyl chloride	1,3-dimethyl-5-isopropylbenzene	208
m-Xylene	*n*-butyl chloride	1,3-dimethyl-5-*sec*-butylbenzene	204
m-Xylene	*tert*-butyl chloride	1,3,-dimethyl-5-*tert*-butylbenzene	29, 158, 166, 169, 204

Table 5.—*Continued*

Aromatic Hydrocarbon Used	Alkyl Halide Used	Compound Formed	Prepared by
m-Xylene	isobutyl bromide	1,3-dimethyl-5-*tert*-butylbenzene	158
p-Xylene	methyl chloride	pseudocumene	151
p-Xylene	ethyl bromide	1,4-dimethyl-2-ethylbenzene	193
o-Xylene	methyl chloride	pseudocumene	151
m-Cymene	*tert*-butyl chloride	*x*-*tert*-butyl-*m*-cymene	161, 170
m-*tert*-Butyltoluene	isopropyl chloride	?-isopropyl-3-*tert*-butyltoluene	160
p-*tert*-Butyltoluene	isopropyl chloride	?-isopropyl-4-*tert*-butyltoluene	160
1,3,5-Trimethylbenzene	methyl iodide	1,2,3,4-tetramethylbenzene	150
1,3,5-Trimethylbenzene	methyl iodide	1,2,3,5-tetramethylbenzene	150, 151
1,3,5-Trimethylbenzene	methyl iodide	1,2,4,5-tetramethylbenzene (durene)	150
1,3,5-Trimethylbenzene	methyl chloride	pentamethylbenzene	151, 155
1,3,5-Trimethylbenzene	methyl chloride	hexamethylbenzene	151
1,2,4-Trimethylbenzene	methyl iodide	1,2,3,4-tetramethylbenzene	150
1,2,4-Trimethylbenzene	methyl iodide	1,2,4,5-tetramethylbenzene (durene)	150
1,2,4-Trimethylbenzene	methyl chloride	1,2,4,5-tetramethylbenzene (durene)	151
1,2,4-Trimethylbenzene	methyl chloride	pentamethylbenzene	155
1,2,4-Trimethylbenzene	methyl chloride	isodurene	151
1,2,3,5-Tetramethylbenzene	methyl chloride	pentamethylbenzene	151
1,2,3,5-Tetramethylbenzene	methyl chloride	hexamethylbenzene	151
Pentamethylbenzene	methyl chloride	hexamethylbenzene	153, 206

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butyl chloride and toluene has been said to result in the formation only of *m-tert*-butyltoluene,[48] a mixture of *m*- and *p-tert*-butyltoluenes,[49] and, in the presence of ferric chloride, only *p-tert*-butyltoluene.[50] Toluene with *n*-butyl chloride and aluminum chloride have been found to give a 3:1 mixture of *m*- and *p-sec*-butyltoluenes.[49]

In other Friedel-Crafts synthesis (*e.g.*, acetylation) the entering substituent usually goes to the *ortho*- or *para*-positions. By preparing sulfoanilides of the products of the reaction of butyl halides with toluene, the following orientation has been ascertained[49]:

[50] M. Bialobrzeski, *Ber.*, 30, 1775-1776 (1897).

Halide	Products	Total Theoretical Yield
n-Butyl chloride	*m-sec*-butyltoluene (75%) *p-sec*-butyltoluene (25%)	45%
Isobutyl bromide	*m-tert*-butyltoluene (70%) *p-tert*-butyltoluene (30%)	30%
tert-Butyl chloride	*m-tert*-butyltoluene (62%) *p-tert*-butyltoluene (38%)	46%

The preponderance of the *m*-derivative in this condensation may be due to the fact that *m*-dialkyl benzenes are quite resistant to rearrangement by aluminum chloride, whereas with *p*-dialkyl derivatives rearrangement is easily effected. Several investigators have, indeed, shown that *p*-xylene is converted into *m*-xylene by treatment with aluminum chloride.[51] Baddeley and Kenner [52] have found that *p*-di-*n*-propylbenzene is converted to the extent of about two-thirds into *m*-di-*n*-propylbenzene by the action of aluminum chloride for two hours at 100°. They state that the rearrangement was affected without isomerization of the alkyl group. The fact that no isomerization occurs during the migration would disprove the possibility that the *meta*-compound may have been formed by primary cleavage of propyl chloride from dipropylbenzene, reaction of the latter with propyl chloride to give 1,3,4-tripropylbenzene, and subsequent cleavage of the 4-propyl group to give 1,3-dipropylbenzene. It is well known that alkylation with propyl chloride is accompanied by isomerization, resulting in the production of isopropyl-substituted derivatives.

It has already been indicated that in the formation of *sym*-trialkyl derivatives upon alkylation of *m*-xylene, the methyl group appears also to have a *meta*-directing effect. It has been suggested by several investigators,[53] that in the production of the 1,3,5-hydrocarbons, the 1,3,4-hydrocarbon is first formed, and that this is subsequently rearranged by the catalyst to the 1,3,5-isomer. Recently, Nightingale and Smith [54] have shown that 1,3-dimethyl-4-butylbenzene rearranges to the 1,3,5-isomer under the influence of aluminum chloride, but that isomerization also occurs during the rearrangement. Isomerization was also indicated in similar treatment of 4-propyl- and 4-amyl-1,3-dimethylbenzenes.

The case against primary *meta*-substitution during alkylation of aromatic hydrocarbons is also borne out by Norris and Rubinstein,[55] who found that at lower temperatures the methyl group has an *ortho*- and *para*-directing effect in condensation of benzene with methyl bromide, but that at higher temperatures *meta*-substitution occurs. It was also shown that higher temperatures are conducive to rearrangement. These factors all point to primary formation of *para*-derivatives in Friedel-Crafts alkylations.

[51] C. M. Mundici, *Gazz. chim Ital.*, **34**, II, 114-124 (1904). R. Heise and A. Tohl, *Ann.*, **270**, 155-171 (1892).
[52] G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303-309 (1935).
[53] C. L. Moyle and L. I. Smith, *J. Org. Chem.*, **2**, 112-137 (1937). A. W. Schorger, *J. Am. Chem. Soc.*, **39**, 2671-2679 (1917).
[54] D. Nightingale and L. I. Smith, *J. Am. Chem. Soc.*, **61**, 101-103 (1939).
[55] J. F. Norris and D. Rubinstein, *J. Am. Chem. Soc.*, **61**, 1163-1170 (1939).

In Friedel-Crafts reactions, substitution in the benzene ring is influenced by the substituents already present. Here, as in other reactions involving substitution in the benzene ring, the electronegativity of the aromatic component is a decisive factor in the course of the reaction.[56]

Di- or poly-substitution rarely occurs in Friedel-Crafts ketone synthesis because of the inhibiting effect of the primarily introduced acyl group. In Friedel-Crafts alkylation, however, the introduced alkyl group has an activating effect, so that, especially with the lower alkyl halides, poly-substitution is the rule. As the carbon chain of the alkyl halide is increased, however, the aromaticity of the primarily formed mono-alkyl benzene decreases. It may be expected, therefore, that poly-substitution would be less common in alkylation of benzene with the higher alkyl halides, for example, lauryl chloride, than it is with the lower alkyl halides.

According to Calloway,[57] the order of reactivity of alkyl halides in Friedel-Crafts alkylations is F > Cl > Br > I, and is exactly opposite to the order of reactivity found for Friedel-Crafts acylations. Calloway states that *n*-butyl iodide did not react with benzene in eighteen hours in the presence of aluminum chloride at 29°, although the other halides reacted rapidly at lower temperatures. This is in accordance with previous findings of Smith and Dobrovolny,[58] who found that methyl chloride gave better results in the methylation of xylene than did the corresponding bromide or iodide.

The course of the reaction of benzene or of its homologs with lower alkyl halides has been a subject of much study ever since 1877, when Friedel and Crafts reported the methylation of benzene.[59] These workers obtained toluene and other methyl derivatives by simply passing a current of methyl chloride into benzene mixed with aluminum chloride and heating gently. Hydrogen chloride was evolved; and upon treating the product with water and then fractionating the resulting product a considerable quantity of toluene, boiling at near 111°, was obtained, as well as the much higher-boiling products, xylene (b.p. 137°), mesitylene (b.p. 163°), durene or tetramethylbenzenes (b.p. 190°), and pentamethyl- and hexamethylbenzene, boiling even higher.

In an early study of the methylation of benzene it has been observed that the methylation of the lower hydrocarbon proceeded much more slowly than that of the higher homologs.[60] For example, when toluene was methylated, about half of it was recovered unchanged; whereas in the methylation of mesitylene the reaction proceeded rapidly with conversion into higher homologs, and no unchanged hydrocarbon was obtained. The methylation of pseudocumene proceeded as rapidly and as completely. Durene and isodurene were very easily converted into penta- and hexa-methylbenzene.

[56] *cf.* M. S. Kharasch and R. Marker, *J. Am. Chem. Soc.*, 48, 3130-3143 (1926). M. S. Kharasch and A. L. Flenner, *J. Am. Chem. Soc.*, 54, 674-692 (1932).
[57] N. O. Calloway, *J. Am. Chem. Soc.*, 59, 1474-1479 (1937).
[58] L. I. Smith and F. J. Dobrovolny, *J. Am. Chem. Soc.*, 48, 1413-1419 (1926).
[59] C. Friedel and J. M. Crafts, *Compt. rend.*, 84, 1392-1394 (1877); *J. Chem. Soc. Abs.*, 725 (1877).
[60] O. Jacobsen, *Ber.*, 14, 2634-2639 (1881).

As a result of the action of methyl chloride on toluene, Jacobsen reported the formation of *o*-, *p*-, and *m*-xylene, pseudocumene and mesitylene, durene and isodurene, and penta- and hexamethylbenzene. Ador and Rilliet [61] stated, however, that no *o*-xylene was formed. Anschütz and Immendorff [62] also studied the course of the reaction which they outlined as follows:

Initial Hydrocarbon	Addition Product	Decomposition Product
Toluene	*p*-xylene *m*-xylene	benzene
p-Xylene	1,3,4-trimethylbenzene	toluene
m-Xylene	1,3,5-trimethylbenzene	toluene
1,3,4-Trimethylbenzene	1,3,4,6-tetramethylbenzene	*p*-xylene, *m*-xylene
1,3,5-Trimethylbenzene	1,3,4,5-tetramethylbenzene	*p*-xylene, *m*-xylene
1,3,4,6-Tetramethylbenzene	pentamethylbenzene	1,3,4-trimethylbenzene
1,3,1,5-Tetramethylbenzene	pentamethylbenzene	1,3,5-trimethylbenzene
Pentamethylbenzene	hexamethylbenzene	1,3,4,6-tetramethylbenzene 1,3,4,5-tetramethylbenzene
Hexamethylbenzene		pentamethylbenzene

They show that, because of this continuation of reactions, the nature of the final product is determined not only by the amount and quality of aluminum chloride but also by the reaction time and temperature. Higher temperatures and longer reaction times result in the formation of higher-alkylated benzenes.

That the formation of higher alkylated benzenes is a function of reaction time was substantiated in a study made on the methylation of xylene.[63] Twenty g of aluminum chloride was added to 1 mole of xylene and a constant stream of methyl chloride was passed through the mixture, which was kept at 95°. The hydrogen chloride formed was determined and the unreacted xylene recovered. The amount of tri- and tetramethylbenzene formed was calculated from the hydrogen chloride evolved, since there were no higher-alkylated bodies present. The amount of penta- and hexamethylbenzene formed with increased reaction time was determined by isolation of the compounds. By plotting the moles of each methylation compound formed against the time of reaction, curves were obtained which indicated successive unimolecular reactions, and not simultaneous ones. It was thus shown that in the Friedel-Crafts reaction only one radical at a time is substituted. The amount of trimethylbenzene formed began to diminish after about three hours, and that of

[61] E. Ador and A. Rilliet, *Ber.*, 11, 1627-1630 (1878).
[62] R. Anschütz and H. Immendorff, *Ber.*, 18, 657-662 (1885); *J. Chem. Soc. Abs.*, 48, 769 (1885)
[63] H. Clement and J. Savard, *Compt. rend.*, 206, 610-612 (1938); *C. A.*, 32, 3760. H. Clement, *Ann. chim.*, 13, 243-316 (1940); *C. A.*, 34, 5830.

tetramethylbenzene after about eight hours. After about six hours a greater amount of tetra- than of trimethylbenzene was present. The amount of pentamethylbenzene exceeded the amount of tetramethylbenzene after about thirteen hours. After twenty-one hours of methylation, there was obtained about 17 per cent each of hexa- and tetramethylbenzene and about 60 per cent of pentamethylbenzene.

In the condensation of methyl or ethyl halides with benzene the polyalkylated hydrocarbons formed are also determined largely by the molecular ratio of the benzene and aluminum chloride used.[64]

In the production of *sym*-triethylbenzene, Gustavson [65] had reported the formation of a complex $Al_2Cl_6,C_6H_3(C_2H_5)_3$. Using the proportion of reactants indicated in Gustavson's formula, Norris and Rubinstein [66] obtained a 90 per cent yield of *sym*-triethylbenzene. They reacted, under cooling, 1 mole of aluminum chloride (Al_2Cl_6), 1 mole of benzene, and 3 moles of ethyl bromide. With ethyl chloride in the same molecular proportion, the yield of *sym*-trimethylbenzene was 83.5 per cent.

The effect of the change in molecular ratios of the reactants on the products obtained was further studied in a series of runs in which varying proportions of the catalyst and alkyl halide were used with one mole of benzene. The results obtained are of sufficient interest to warrant reproduction. Figures in the following table indicate the moles of reactants and products formed per mole of benzene:

No. of Expt.	1	2	3	4	5	6
C_2H_5Br	3.06	3.06	3.1	4.2	2.06	1.05
Al_2Cl_6	1.05	0.52	0.17	1.0	0.35	0.35
Products Formed						
$C_6H_5C_2H_5$	..	016	066	....	.17	.08
$C_6H_4(C_2H_5)_2$	0.016	02	.09	. ..	.06	.11
$C_6H_3(C_2H_5)_3$	.93	79	.17	79	.53	.24
$C_6H_2(C_2H_5)_4$	.018	.10	11	17	.01	.005
$C_6H(C_2H_5)_5$	....	....	.11	02	. .	....
$C_6(C_2H_5)_6$	....	....	.02	..	....	. ..

According to Norris, these results show clearly that the ratio of benzene to aluminum chloride is the determining factor in the production of the trialkylated product, and that the ratio of alkyl halide to benzene has comparatively little effect. These conclusions, however, do not seem to be substantiated in Experiments 5 and 6.

Practically the same result was obtained with ethyl chloride; using the mole ratio 1 C_6H_6, 3 C_2H_5Cl, 1 Al_2Cl_6, the yield of 1,3,5-triethylbenzene was 83.5 per cent. Ethylation of toluene and of xylene, using molar proportions of hydrocarbon to aluminum chloride, similarly gave good yields of symmetrically substituted trialkylbenzenes.

However, in reacting methyl bromide with benzene at 0°, and using a

[64] J. F. Norris and J. N. Ingraham, *J. Am. Chem. Soc.*, **60**, 1421-1423 (1938). For a study of the influence of amount of ethyl chloride used, see L. I. Smith and C. O. Guss., *J. Am. Chem. Soc.*, **62**, 2625-2629 (1940).

[65] G. Gustavson, *Compt. rend.*, **136**, 1065-1067 (1903); *J. Chem. Soc. Abs.*, **84**, I, 470-471 (1903).

[66] J. F. Norris and D. Rubinstein, *J. Am. Chem. Soc.*, **61**, 1163-1170 (1939).

C_6H_6-CH_3Br-Al_2Cl_6 ratio of 1:3:1, the chief product is 1,2,4-trimethylbenzene. In order to study the orienting effect of the methyl group, toluene was reacted with methyl halides under conditions leading to maximum conversion to xylenes. Temperatures of −3 to 106° were used. At lower temperatures the methyl group had an *ortho-para* effect; at higher temperatures *meta*-substitution occurred. Thus at 0° when methyl chloride was used, the xylenes formed contained 27.3 per cent of the *meta*- and 53.5 per cent of the *ortho*-isomer; at 106°, 98.2 per cent *meta*- and 1.8 per cent *ortho*-.

Accordingly, the rearrangement of *o*- and *p*-xylene under the conditions employed in the methylation of toluene was studied, and it was shown that higher temperatures (55°) induced some rearrangement to the *meta*-isomer.

This indicated that reaction of a *meta*-xylene-aluminum chloride complex at higher temperatures would yield chiefly 1,3,5-trimethylbenzene. Using technical *meta*-xylene (containing about 61 per cent *m*-xylene) and commercial aluminum chloride, a complex was prepared by adding 540 g of the aluminum chloride to 212 g of the xylene at 120°. When the temperature had dropped to 100°, 91 g of methyl chloride was introduced during a period of from 30 to 60 minutes. No hydrogen chloride was evolved until about two-thirds of the methyl chloride had been added. The yield of mesitylene, calculated on the methyl chloride, was 63 per cent of the theoretical.

These methods, based on the use of the proportion of reactants expressed in hydrocarbon-aluminum halide complexes, have given much better yields of purer symmetrical trialkylderivatives than had been previously obtained.

According to Boedtker and Halse,[67] the formation of monoalkyl derivatives in the Friedel-Crafts reaction is favored when a relatively large amount of benzene is used in the presence of a small quantity of aluminum chloride; on the other hand, small amounts of benzene and large amounts of aluminum chloride favor the formation of polyalkyl derivatives. When large quantities of benzene are used, it would be expected that the hydrocarbon acts as diluent, thus mitigating the possibility of poly-alkylation.

This influence of the proportion of reactants in alkylation of benzene with ethyl or isopropyl chloride has also been investigated by Wertyporoch and Firla.[68] Ethylbenzene was found to be obtained in about 42 per cent yield from 0.25 mole of benzene, 1.5 moles of ethyl chloride, and 0.1 mole of aluminum chloride. Increase in the amount of aluminum chloride caused less of the mono-derivative and more of the diethyl derivative to be formed.

From 1 cc of benzene, 10 cc of isopropyl chloride, and 1.3 g of aluminum chloride, a yield of 0.2 g of a tetraisopropylbenzene, melting at 117-118°, has been reported. Reacting 2 cc of dipropylbenzene with 50

[67] E. Boedtker and O. M. Halse, *Bull. soc. chim.*, 19, 444-449 (1916); *C. A.*, 11, 938.
[68] E. Wertyporoch and T. Firla, *Ann.*, 500, 287-295 (1933).

cc of propyl chloride and 0.74 g of aluminum chloride gives 0.3 g of hexapropylbenzene.

Other methods for accelerating alkylation and improving yields have been investigated. Thus it has been found that the yield of ethylbenzene may be increased by using more than the necessary amount of solvents, for example, benzene.[69] It may be further improved by treating the higher-boiling products with benzene and aluminum chloride, thus converting them to less alkylated benzenes.

The retreatment of higher-boiling products in the ethylation of benzene is the subject of a patent to Naugatuck Chemical Company [70] Here the dark-brown, oily mass which separates from the first run in which benzene, ethyl chloride and aluminum chloride had been used, is treated with small quantities of aluminum to bring about reactivation. The entire process may involve seven consecutive runs, with addition of aluminum in the second and fifth runs.

The preparation of polymethylbenzenes by methylation of technical xylene has been studied by Smith and co-workers.[71] Methyl bromide, methyl iodide, and methyl chloride were investigated as methylating agents, and it was found that methyl chloride gave best results. With a xylene having a distilling range of 135-140°, the alkylation with methyl chloride and aluminum chloride takes place readily, and may be easily controlled so that trimethylbenzenes, tetramethylbenzenes, or pentamethylbenzenes constitute the main products. It was found that the mixture of tetramethylbenzenes was rich in durene, which could be isolated by cooling to about −10° and filtering it off. Moreover, more durene could be secured from the filtrate by warming the latter with fresh aluminum chloride. By working over these filtrates, a 35 per cent yield of durene, based on the original xylene, was obtained.

Pentamethylbenzene in 33 per cent yield, based on the original xylene, was obtained by continuing methylation beyond the tetramethylbenzene stage.

By rapid methylation of pentamethylbenzene a 30 per cent yield of pure hexamethylbenzene, based on the penta-compound used, was secured.

It has been found that 1,2,3-trimethylbenzene is not formed in the reaction of xylene with methyl chloride and aluminum chloride. This compound is easily obtained, however, by simply refluxing xylene with aluminum chloride.[72]

Work on the separation of the products resulting from the methylation of commercial xylene has been in progress.[73] Most of it has consisted in

[69] C. Radziewanowski, *Ber.*, **27**, 3235-3238 (1894); *J. Chem. Soc. Abs.*, **68** (1), 120 (1895).

[69a] C. H. Milligan and E. E. Reid, *J. Am. Chem. Soc.*, **44**, 206-210 (1922); for revivification of catalyst by adding fresh aluminum chloride to reaction mixture, see U. S. P. 2,222,012 (1940), U. S. P. 2,198,595 (1940) to Dow Chemical Co.

[70] British P. 259,507 (1926) to Naugatuck Chemical Co.; *C. A.*, **21**, 3370 (1927); *cf.* Canadian P. 265,521 (1926) to M. G. Shepard; *C. A.*, **21**, 917.

[71] L. I. Smith and F. J. Dobrovolny, *J. Am. Chem. Soc.*, **48**, 1413-1419 (1926).

[72] L. I. Smith and O. W. Cass, *J. Am. Chem. Soc.*, **54**, 1603-1609 (1932); *C. A.*, **26**, 2714.

[73] L. I. Smith and F. H. MacDougall, *J. Am. Chem. Soc.*, **51**, 3001-3008 (1929). L. I. Smith and A. R. Lux, *J. Am. Chem. Soc.*, **51**, 2994-3000 (1929). F. H. MacDougall and L. I. Smith, *J. Am. Chem. Soc.*, **52**, 1998-2001 (1930). L. I. Smith and A. P. Lund, *J. Am. Chem. Soc.*, **52**, 4144-4150 (1930). L. I. Smith and C. O. Guss, *J. Am. Chem. Soc.*, **62**, 2635-2638, 2630-2631, 2631-2635 (1940).

preparing variously methylated benzenes for the determination of their physical properties.

Mixtures of the three xylenes may be analyzed by a freezing point method.[74] Earlier workers have separated alkylation products through their sulfonates[75] or their sulfanilides.[76]

The influence of reaction conditions is especially apparent in condensations effected with alkyl halides higher than ethyl, for here possible isomerization and cleavage of the alkyl group are to be avoided.

Like the methyl and ethyl halides, propyl halides react with benzene in the presence of aluminum chloride with formation of various substituted benzenes. In the presence of aluminum chloride the propyl group is converted to isopropyl[77]; therefore, in preparing isopropylbenzene, it is immaterial whether propyl or isopropyl halide is employed. Isomerization occurs almost invariably. As in all Friedel-Crafts reactions, however, the amount of catalyst used, the temperature employed and the duration of the reaction regulates the type of substitution; so that under mild conditions, *n*-propyl halide and benzene yields a mixture of *n*- and isopropylbenzenes. This is especially true in the presence of 8 per cent by weight or less of aluminum chloride with respect to the *n*-propyl-bromide used.[78] However, 53 g of *m*-xylene with 20 g of isopropyl chloride or the same amount of *n*-propyl chloride in the presence of 15 g of aluminum chloride results in the formation of 1,3-dimethyl-5-isopropylbenzene in 48 and 46 per cent yields, respectively.[79]

An 18 per cent yield of tetraisopropylbenzene was secured from isopropyl chloride, benzene, and aluminum chloride at 0°, in a reaction period of not more than five minutes.[80] If the tetra-alkylbenzene is left at room temperature with aluminum chloride for two hours, it undergoes decomposition to tri-, di- and mono-isopropylbenzene.

The reaction of butyl halides with benzene in the presence of aluminum chloride results in the formation of iso-, *sec*- and *tert*-butylbenzenes, due to branching caused by the catalyst.

Gossin[81] reported the production of two liquids of the formula $C_{10}H_{14}$, in the reaction of isobutyl chloride with benzene. One boiled at 166-167°; the other, formed in only very small quantities, boiled at 152-155°. Isobutylbenzene boils at 167°. A 50 per cent theoretical yield of *sec*-butylbenzene was secured by Schramm,[82] who reacted *n*-butyl chloride with benzene and aluminum chloride. Estreicher[83] obtained a 95 per cent yield of butylbenzenes (a mixture of *n*- and *sec*-butylbenzenes) by varying the proportion of the reactants used. Thus he used 1½ moles of primary *n*-butyl chloride with a large excess of benzene (about 9 moles)

[74] J. F. Norris and D. Rubinstein, *J. Am. Chem. Soc.*, 61, 1163-1170 (1939).
[75] *Cf.* O. Jacobsen, *Ber.*, 21, 2814-2829 (1888).
[76] J. B. Shoesmith and J. F. McGechen, *J. Chem. Soc.*, 2231-2236 (1930).
[77] G. Gustavson, *Ber.*, 13, 157-159 (1880); *J. Chem. Soc. Abs.*, 370 (1880).
[78] P. Genvresse, *Compt. rend.*, 116, 1065-1067 (1893); *J. Chem. Soc. Abs.*, 64 (1), 505 (1893).
[79] D. Nightingale and B. Curtin, *J. Am. Chem. Soc.*, 62, 280-3 (1940).
[80] T. Fuls, *Roczniki Chem.*, 14, 87-92 (1934); *C. A.*, 28, 6426.
[81] E. Gossin, *Bull. soc. chim. (2)*, 41, 446-447 (1884); *J. Chem. Soc. Abs.*, 1312 (1884).
[82] J. Schramm, *Monatsh.*, 9, 613-625 (1888).
[83] T. Estreicher, *Ber.*, 33, 430-443 (1900); *J. Chem. Soc. Abs.*, 78 (1), 213 (1900).

and only ⅛ mole of aluminum chloride (in the form of a mixture of pulverized aluminum and mercuric chloride). Even the small amount of aluminum chloride thus present resulted in some isomerization.

Using a similar procedure, the preparation of *sec*-butylbenzene, boiling at 173.2-174.2°, from benzene and *sec*-butyl chloride was effected with an 82.5 per cent theoretical yield.

tert-Butyl chloride was condensed with benzene in the presence of aluminum chloride by Boedtker.[84] The sole product was *tert*-butylbenzene, boiling at 168.2°. In reacting a mixture of isobutyl and *tert*-butyl chlorides with benzene, the same author reported the formation principally of *tert*-butylbenzene, with small amounts of iso-, *sec*- and *n*-butylbenzenes.

That the type of substitution is a function of the time and temperature of the reaction is shown by the fact that di-isobutylbenzene is produced from butyl chloride, benzene, and aluminum chloride at 0° in ninety seconds. If, however, the reaction mixture is left for some time at room temperature, tri-isobutylbenzene, butylbenzene, and an unidentified product are formed.[85]

The preparation of butylxylene is of practical importance in the perfume industry in the manufacture of xylene musk. The reaction of *tert*-butyl chloride with *m*-xylene and aluminum chloride results only in low yields of 5-*tert*-butyl-1,3-xylene. It has been found, however, that if a stream of isobutylene gas is led through a mixture of *m*-xylene, dry aluminum chloride, and a little isobutyl chloride, a series of reactions (intermediate formation of *tert*-butyl chloride and subsequent condensation with *m*-xylene) occurs which results in almost theoretical yields of 5-*tert*-butyl-1,3-xylene. The hydrogen chloride freed during the reaction with the small amount of isobutyl chloride initially present chlorinates the incoming butylene.[86]

In another method, a 90-94 per cent yield of 5-*tert*-butyl-1,3-xylene, of such purity that it may be used directly in musk xylene manufacture, is claimed to be produced if alkylation is conducted at a temperature below 50°, and in the presence of not over 2 per cent by weight of aluminum chloride. It is indicated that, in the reaction of *m*-xylene with *tert*-butyl chloride, diminishing the temperature or decreasing the amount of catalyst discourages the formation of by-products without seriously affecting the yield of the main product.[87]

Higher alkylbenzenes have been prepared for a variety of commercial applications. For the preparation of textile assistants Seidel and Engelfried[88] obtained octadecylbenzene from *n*-octadecyl bromide, benzene, and aluminum chloride. This was easily changed into octadecylbenzenesulfonic acid, whose sodium salt was found to be a textile aid.

Higher paraffin hydrocarbons, for example, a kerosene fraction corre-

[84] E. Boedtker, *Bull. soc. chim.* (3), 31, 965-971 (1904); *J. Chem. Soc. Abs.*, 86 (1), 801 (1904)
[85] T. Fuda, *Roczniki Chem.*, 14, 87-92 (1934), *C. A.*, 28, 6426
[86] O. Gerhardt *Reichstoffind*, 5, 67-69 (1930); *C. A.*, 24, 4897; *cf.* German P. 184,230 to Agfa.
[87] U. S. P. 2,023,566 (1935) to W. V. Wirth (to E. I. du Pont); *C. A.*, 30, 738.
[88] F. Seidel and O. Engelfried, *Ber.*, 69, 2567-2591 (1936); *Brit. Chem. Abstracts*-B, 116 (1937).

sponding to dodecane, may be chlorinated to produce a mixture of unreacted paraffin hydrocarbons and the corresponding alkyl chloride. This is then submitted to a splitting reaction and the alkyl chloride and olefin of the mixture is condensed with an aryl hydrocarbon, like benzene, for the formation of alkyl-substituted aryl hydrocarbon derivatives.[89] The mixture of the paraffin material and the alkyl mono-chloride may be condensed with the aryl hydrocarbon, and the uncondensed material separated by distillation.[90]

Mineral oil fractions may be chlorinated and then condensed with benzene or other aromatic hydrocarbons in the presence of aluminum chloride After purification by distillation the products are sulfonated for the preparation of wetting and cleansing agents.[91]

In a process for the preparation of sulfonated condensation products, 385 parts (by weight) of a chlorinated light petroleum fraction is caused to react with a suspension of 10 parts of aluminum chloride in 350 parts of xylene at 50°. The resulting alkylated xylene is subsequently sulfonated.[92]

Kerosene cuts of narrow boiling ranges, corresponding to the boiling points of nonane, decane, undecane, dodecane, tridecane, tetradecane, and pentadecane, respectively, may be chlorinated so as to produce a preponderant proportion of alkyl mono-chlorides; and the alkyl halides thus obtained may be used for alkylation of hydrocarbons of the benzene series.[93]

Lubricants of high viscosity are obtained by condensing chlorinated paraffins, especially of from 11 to 25 carbon atoms (petroleum distillates or products of Fischer-Tropsch benzine synthesis) with aromatic hydrocarbons in the presence of aluminum chloride. A fuller review of work in the preparation of these "pour-point" depressors will be given in the chapter on aluminum chloride in the petroleum industry.

The production of deuterobenzene by the reaction of benzene with deuterium chloride in the presence of aluminum chloride is really a type of Friedel-Crafts reaction, the deuterium chloride playing the role of an alkyl halide to give a hexa-substituted benzene[94]:

$$C_6H_6 + 6DCl \rightleftharpoons C_6D_6 + 6HCl$$

For the production of alkylated aromatic ketones, the alkylating agent and the acylating agent may be condensed with an aromatic hydrocarbon in the same reaction mixture.[95] For example, a 60 per cent yield of *p*-amylacetophenone is obtained by treating a solution of amyl chloride, benzene, and acetic anhydride in ethylene dichloride with aluminum chloride. Without the use of the solvent, the yield is only 30 per cent.

[89] U. S. P. 1,995,827 to C. A. Thomas (to Sharples Solvents Corp.) (1935)
[90] U. S. P. 2,072,061 (1937) to C. A. Thomas (to Sharples Solvents Corp.); *C. A.*, 31, 2613 (1937)
[91] British P. 416,879 (1934) to I. G. Farbenindustrie
[92] German P. 647,988 (1937) to I. G. Farbenindustrie
[93] U. S. P. 2,161,178-4 (1939) to L. P. Kyrides (to Monsanto Chemical Co.)
[94] A. Klit and A. Langseth, *Z. physik. Chem.*, A176, 65-80 (1936); *Brit. Chem. Abstracts*-A, 714 (1936); *C. A.*, 30, 5091 (1936).
[95] U. S. P. 2,004,069 (1935) to H. A. Bruson and O. Stein (to Rohm and Haas Co.)

Concurrent (or rather consecutive) acylation-alkylation reactions require more than one mole of aluminum chloride; otherwise acylation usually occurs.[96]

Isomerization Accompanying Friedel-Crafts Reactions*

Isomerization of an alkyl residue usually occurs during Friedel-Crafts alkylation. Wertyporoch and Firla [35] have found that propyl chloride is converted by large amounts of aluminum chloride into isopropyl chloride, hydrogen chloride, and condensation products. The conversion of propyl-bromide into isopropyl bromide by the action of aluminum bromide had been noted by Kekulé and Schrötter in 1880.[36] According to Schramm [37] the production of tertiary butylbenzene from isobutyl halide, benzene, and aluminum chloride was assumed to be due not to a preliminary isomerization of the alkyl halide, but to dehydrohalogenation, followed by addition of benzene to the double bonds of the resulting olefin. Thus, isobutyl chloride was found to split into butylene and hydrogen chloride by the action of aluminum chloride. Addition of the benzene would thus result in formation of *tert*-butylbenzene, the phenyl group attaching itself to the carbon atom which possesses the least hydrogen:

$$(CH_3)_2 . CH . CH_2Cl \xrightarrow{AlCl_3} (CH_3)_2 . C : CH_2 + HCl$$

$$(CH_3)_2 . \underset{\cdot\cdot}{C} + C_6H_6 \xrightarrow{AlCl_3} (CH_3)_2\overset{\cdot}{C} . C_6H_5$$
$$\quad\quad\quad

$$\text{1,3-dimethyl-4-}n\text{-butylbenzene} \xrightarrow{AlCl_3} \text{1,3-dimethyl-5-}sec\text{-butylbenzene}$$

$$\text{1,3-dimethyl-4-}sec\text{-butylbenzene} \xrightarrow{AlCl_3} \text{1,3-dimethyl-5-}tert\text{-butylbenzene}$$

Here an attempt was made to explain the isomerization of the *n*-butyl radical by applying Whitmore's[39] theory of intramolecular rearrangements:

$$(CH_3)_2C_6H_3(C_4H_9) \xrightarrow{AlCl_3} (CH_3)_2C_6H_3^- + CH_3{-}CH_2{-}CH_2{-}CH_2^+$$

$$CH_3{-}CH_2{-}CH_2{-}CH_2^+ \xrightarrow[\text{shift}]{H:} CH_3CH_2{-}{-}{}^+CHCH_3$$

With the *sec*-butyl ion similar shifting of the proton would account for formation of the *tert*-butyl ion:

$$CH_3CH_2^-{-}{}^+CHCH_3 \xrightarrow[\text{shift}]{CH_3:} {}^+CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3 \xrightarrow[\text{shift}]{H:} CH_3{-}{}^+\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3$$

In the reaction of isoamyl chloride with benzene and aluminum chloride the formation of three amylbenzenes has been noted[40]:

(1) $(CH_3)_2CH\,.\,CH_2CH_2\,.\,C_6H_5$

(2) $(CH_3)_2CH\overset{\displaystyle H}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\,.\,C_6H_5$

(3) $(CH_3)_2\overset{\displaystyle H}{\underset{\displaystyle CH_2CH_3}{\overset{|}{\underset{|}{C}}}}\,C_6H_5$

Here branching of the isoamyl radical occurs:

$$(CH_3)_2CHCH_2CH_2{-} \longrightarrow (CH_3)_2CH\overset{\displaystyle H}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}{-}$$

$$(CH_3)_2CHCH_2CH_2 \longrightarrow (CH_3)_2(C_2H_5)C{-}$$

If branching were due merely to removal of hydrogen chloride, and attachment of the benzene at the resulting unsaturated linkage, only product (2) would have been formed in the reaction. A shifting of the proton would explain the formation of both product (2) and product (3). The production also of isoamylbenzene may be interpreted as an indication of the fact that isoamyl chloride is not completely converted to isomerides during Friedel-Crafts reaction with benzene.

Another case in which Friedel-Crafts alkylation with alkyl halides has led to formation of an unisomerized derivative has been reported by

[39] F. C. Whitmore, *J. Am. Chem. Soc.*, **54**, 3274-3283 (1932).
[40] M. Konowaloff and J. Egoroff, *J. Russ. Phys.-Chem. Soc.*, **30**, 1031-1035 (1898); *C. Z.*, **1899**, I, 776-777

Genvresse [41] who secured a mixture of *n*- and isopropylbenzenes in the reaction of *n*-propyl bromide with benzene and aluminum chloride. He indicated that the ratio of the unisomerized product is probably a function of the quantity of catalyst used, increasing amounts of catalyst resulting in increasing proportions of isopropylbenzene in the reaction mixture.

Ipatieff and his co-workers [42] note the influence of temperature upon isomerization accompanying alkylation. At −6°, *n*-propyl chloride with benzene and aluminum chloride yields monopropylbenzene consisting of 60 per cent of *n*-propylbenzene and 40 per cent isopropylbenzene; at 35°, there is obtained 40 per cent *n*-propyl- and 60 per cent of isopropylbenzene. This may be due to the fact that at lower temperatures alkylation occurs through the formation of an alkyl halide-aluminum chloride complex and at higher temperatures through primary dehydrohalogenation of the alkyl halide to olefin and subsequent addition at the double bond. Firla [43] notes that if reaction of butyl chloride with benzene and aluminum chloride is effected at 0° for ninety seconds, the product is dibutylbenzene, but that when the reaction mixture is left at room temperature migration of the alkyl groups occurs.

The production of *n*-propylbenzene in the reaction of allyl chloride with benzene and aluminum chloride has been ascribed [44] to hydrogenation of intermediately formed β-chloropropylbenzene. If alkylation is accompanied by dehydrohalogenation and union of benzene at the olefinic linkage, the formation of *n*-alkylbenzenes in the Friedel-Crafts reactions noted above can be explained only by a series of reversible intramolecular changes within the alkyl residue, or by cleavage and addition of fragments to form the straight-chain residue.

Isomerization of the alkyl group during Friedel-Crafts reaction with alkyl halides seems in no way to be affected by the nature of the aromatic component. Since, for example, reaction of isobutyl chloride with benzene, alkylated benzenes, phenols, or ethers, results in formation of *tert*-butyl derivatives,[45] increasing activity of the aromatic compound does not prevent the disrupting effect of aluminum chloride on the paraffin chain. If isomerization is independent of alkylation it must, therefore, occur at a greater speed than does alkylation of even highly activated compounds. Data concerning catalytic isomerization of paraffins,* although meager, indicate that velocity of rearrangement of paraffins is less than that of alkylation. At present, too little is known concerning relative velocities of the isomerizing effect and the dehydrohalogenating activity of aluminum chloride on alkyl halides to permit of anything but speculation concerning the mechanism of isomerization accompanying alkylation.

[41] P. Genvresse, *Compt. rend.*, **116**, 1065-1067 (1893); *J. Chem. Soc. Abs.*, **64** (1), 505 (1893).
[42] V. N. Ipatieff, H. Pines, and L. Schmerling, *J. Org. Chem.*, **5**, 253-263 (1940).
[43] T. Firla, *Roczniki Chem.*, **14**, 87-92 (1934); *C. A.*, **28**, 6426.
[44] C. D. Nenitzescu and D. A. Isăcescu, *Ber.*, **66**, 1100-1103 (1933).
[45] See Tables 3, 4, and 5 and M. Konowaloff, *J. Russ. Phys.-Chem. Soc.*, **30**, 1036-1040 (1898); *C. Z.* 1899, I, 777.

* See Chapter 17.

Isomerization has been noted by Nenitzescu and Chicos [40] to occur during the condensation of cyclohexane, *n*-pentane, or *n*-hexane with acetyl chloride. In each case, reaction is shown to proceed through primary isomerization of the paraffin or cycloparaffin, subsequent dehydrogenation, and addition of the acetyl chloride at the unsaturated linkage.

Theories Advanced for Alkylation with Alkyl Halides

The mechanism of reactions catalyzed by anhydrous aluminum chloride forms the subject of Chapter 4, which summarizes theories which have been proposed for explaining a variety of reactions effected by this catalyst. For those who want a more detailed account of work dealing specifically with attempts to explain the mechanism of alkylation with alkyl halides, there is included here a compilation of work which has been directed to this end.

Complexes with hydrocarbons. -The mechanism of reactions effected in the presence of aluminum chloride was assumed by Friedel and Crafts [1] to take place through a primary exchange of hydrogen in the hydrocarbon for an Al_2Cl_5 residue:

$$C_6H_6 + Al_2Cl_6 \longrightarrow C_6H_5.Al_2Cl_5 + HCl$$

The latter compound combined with an aliphatic chloride thus:

$$C_5H_{11}Cl + C_6H_5.Al_2Cl_5 \longrightarrow AlCl_3 + C_6H_5.C_5H_{11}$$

They were unable to isolate the compound $C_6H_5.Al_2Cl_5$. In attempting its preparation Friedel and Crafts prepared aluminum phenyl from mercury phenyl and aluminum, and found that it reacted very much as does benzene in the presence of aluminum chloride, yielding diphenylmethane with benzyl chloride, phenol with oxygen, and diphenylene disulfide and phenyl sulfide with sulfur. They secured no evidence of any reaction of benzene or toluene with either aluminum bromide or aluminum chloride. When hydrogen chloride or water was added to a mixture of benzene with aluminum chloride, however, an oily liquid was produced. Analyses of the liquid obtained in various experiments showed that it was a complex mixture, which was assumed to consist of a chlorohydroxide of aluminum, the organometallic compound $C_6H_5.Al_2Cl_5$, excess of the hydrocarbon, and hydrochloric acid.

At about the same time Gustavson observed [2] the formation of compounds of the type $Al_2Br_6,6C_6H_6$ and $Al_2Br_6,6C_7H_8$ in Friedel-Crafts reactions of benzene or toluene in presence of aluminum bromide. Aluminum chloride was assumed to react analogously.[3] The compounds, secured by passing hydrogen chloride into a suspension of aluminum chloride in benzene or toluene, were rather viscous, slightly orange-colored

[40] C. D. Nenitzescu and I. Chicos, *Ber.*, **68**, 1584-1587 (1935); *C. A.*, **29**, 7279.

[1] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, **14**, 433-472 (1888); *(6)*, **1**, 449-532 (1884); *Compt. rend.*, **100**, 692-698 (1885); **85**, 74-77 (1877); *Ber.*, **22**, Ref. 98 (1889).

[2] G. Gustavson, *Bull. soc. chim. (2)*, **30**, 435 (1878); *J. Rus. Chem. Soc.*, **12**, 1-2 (1880); *C. Z.*, 1880, 584.

[3] G. Gustavson, *Bull. soc. chim. (2)*, **31**, 71 (1879); *Ber.*, **11**, 2151 (1878); **12**, 853 (1879).

liquids which were slightly decomposed upon addition of water, regenerating benzene and toluene. The complex with benzene was reported as $Al_2Cl_6,6C_6H_6$, having a specific gravity of 1.14 at 0°, and that with toluene as $Al_2Cl_6,6C_7H_8$, with a specific gravity of 1.08 at 0°. At lower temperatures the benzene complex solidified into a crystalline mass, m. p. 3°. Although Gustavson [4] had analyzed the compound $Al_2Cl_6,6C_7H_8$, and was quite sure of its existence, he agreed that its formation could not explain those Friedel-Crafts reactions with toluene which take place at high temperatures, for the compound was decomposed by heat. A similar compound, $Al_2Cl_6,3(C_{10}H_{14})$ was prepared from cymene.[5]

A study on the electrolysis and conductivity of compounds of aluminum bromide with benzene or toluene, as prepared by Gustavson, has been made.[6]

Also Walker [7] added small portions of aluminum chloride to mixtures of ethyl bromide and benzene or naphthalene and noted the variation in conductivity. Breaks in the curves indicated the formation of compounds $3X,AlCl_3$, $2X,AlCl_3$, and $X,AlCl_3$, where X stands for a molecule of hydrocarbon. Since readings were taken before evolution of hydrogen bromide was noted, the breaks were not due to alkylation of the hydrocarbon. Varying the proportion of hydrocarbon used gave a corresponding variation in conductivity curves.

Ulich and Nespital [8] report that the dipole moment for aluminum bromide in benzene was found to be 4.89×10^{-18}, and that in dilute benzene solution it was probably present in the form of $AlBr_3C_6H_6$.

Schroeter [9] explains the manifold synthetic, degrading, and rearranging properties of aluminum chloride by assuming the formation of polymolecules, such as $C_6H_6,AlCl_3$ which rearranges intramolecularly into $C_6H_5AlCl_2,HCl$. The hydrogen chloride of this complex is then exchanged for alkyl halide, as methyl chloride; the resulting $C_6H_5AlCl_2,CH_3Cl$ yields toluene and aluminum chloride by normal organo-metallic synthesis.

Recently, Norris and Rubinstein [10] made a study of intermediate compounds formed in Friedel-Crafts hydrocarbon syntheses. These investigators passed dry hydrogen bromide into a solution of 40.5 g of aluminum bromide in toluene at room temperature and found that within twelve minutes reaction leading to the formation of an oil was completed. This material had the composition $Al_2Br_6,6C_6H_5CH_3$. When it was evaporated at room temperature at 10-11 mm pressure, the non-volatile product appeared to have the formula $Al_2Br_6,C_6H_5CH_3$. That hydrogen bromide was necessary for the formation of a complex was shown by the fact that when a mixture of aluminum bromide and toluene in the proportions $Al_2Br_6 + C_6H_5CH_3$ was evacuated under the same conditions,

[4] G. Gustavson, *J. prakt. Chem (2)*, 42, 501-507 (1890)
[5] G Gustavson, *Ber.*, 12, 694-695 (1879).
[6] W Nemmaki and W Plotnikow, *J Russ. Phys.-Chem Soc.*, 40, 391-396 (1908), *C. Z.*, 1908, II 1505. W. Plotnikow, *J. Russ. Phys.-Chem. Soc.*, 40, 1247-1257 (1908), *C. Z.*, 1909, I, 492-493.
[7] J. W. Walker, *J. Chem. Soc.*, 85, 1082-1098 (1904).
[8] H. Ulich and W. Nespital, *Z. Elektrochem.*, 37, 559-563 (1931).
[9] G Schroeter, *Ber.*, 57, 1990-2003 (1924); *C. A.*, 19, 1270
[10] J F Norris and D. Rubinstein, *J. Am Chem. Soc.*, 61, 1163-1170 (1939).

crystals of aluminum bromide separated out, and at the end of one hour all the hydrocarbon had been removed.

The molecular weight of the oil secured from aluminum bromide, toluene, and hydrogen bromide was determined cryoscopically in *p*-dichlorobenzene, and found to be 174. If the components of the oil had affected the freezing point separately, the molecular weight would have been 155. The molecular weight of $Al_2Br_6,C_6H_5CH_3$ is 181. Obviously the oil primarily formed, having the composition $Al_2Br_6,6C_6H_5,CH_3$, is readily decomposed, yielding probably the stable complex Al_2Br_6, $C_6H_5CH_3$.

Complex formation of toluene with aluminum chloride could not be so carefully studied because of aluminum chloride being only slightly soluble in toluene. An oil was prepared from aluminum chloride, toluene, and hydrogen chloride, and although analytical data showed that a pure compound had not been obtained, indications were that a mixture of compounds had been formed and that the ratio of the Al_2Cl_6 in them to hydrocarbon was 1 to 6.

Later, Norris and Ingraham [11] prepared the crystalline compound, $Al_2Br_6,2C_6H_5(C_2H_5)_3,HBr$, m.p. 64-66°, by passing hydrogen bromide into a solution of aluminum bromide in *sym*-triethylbenzene. The analogous complex, $Al_2Cl_6,2C_6H_3(C_2H_5)_3,HCl$, prepared by covering freshly sublimed aluminum chloride with the hydrocarbon and passing in hydrogen chloride, was secured as an oil which upon cooling changed to crystals melting at 48-49°. A crystalline complex was also prepared from aluminum bromide and hydrogen bromide with pseudocumene. The complexes from toluene or benzene, however, were rather unstable oils, the stability of the complexes increasing as the number of alkyl groups present increases.

In further work on intermediate complexes in the Friedel and Crafts reaction Norris and Wood [12] prepared complexes in which the hydrogen halide was replaced by the alkyl halide. Thus, $Al_2Br_6,s\text{-}C_6H_3(CH_3)_3$, C_2H_5Br was prepared by shaking together a mixture of mesitylene, ethyl bromide and aluminum bromide at 0°. However, attempts to prepare complexes of definite composition containing *only* hydrocarbon and aluminum halide were unsuccessful, and it was concluded that the presence of a third component seems to be necessary for the formation of an isolable complex.

Recent work of Norris and his co-workers [13] indicates that the relative proportion of aluminum chloride to hydrocarbon is a determining factor in the orientation of alkyl groups in Friedel-Crafts alkylations with alkyl halides [14] and with alcohols.[15] Using the proportion of reactants indicated in the additive complex, $Al_2Cl_6,C_6H_3(C_2H_5)_3$, which had been

[11] J. F. Norris and J. N. Ingraham, *J. Am. Chem. Soc.*, 62, 1298-1301 (1940).
[12] J. F. Norris and J. E. Wood, *J. Am. Chem. Soc.*, 62, 1428-1432 (1940).
[13] J. F. Norris and J. N. Ingraham, *J. Am. Chem. Soc.*, 60, 1421-1423 (1938). J. F. Norris and D. Rubinstein, *J. Am. Chem. Soc.*, 61, 1163-1170 (1939). J. F. Norris and B. M. Sturgis, *J. Am. Chem. Soc.*, 61, 1413-1417 (1939).
[14] J. F. Norris and D. Rubinstein, *loc. cit.*
[15] J. F. Norris and J. N. Ingraham, *loc. cit.* J. F. Norris and B. M. Sturgis, *loc. cit.*

reported by Gustavson [16] as a product of the reaction of ethyl chloride with benzene in presence of aluminum chloride, Norris and Rubinstein [14] obtained 83.5-90 per cent yields of *sym*-triethylbenzene. That the yield of triethylbenzene secured, however, is determined largely by the amount of aluminum chloride used, the molecular ratio of benzene to ethyl bromide having a relatively small effect, was shown by the fact that varying the amount of the alkyl halide used from 1.05 to 4.2 moles gave *sym*-triethylbenzene in 69-79 per cent yields, whereas lowering the proportion of the catalyst gave products in which all possible ethyl derivatives were present.

Menschutkin [17] previously reported, however, that thermal analysis indicates that aluminum bromide forms no complex with benzene, toluene, or *p*-xylene. The melting point curves of mixtures of aluminum bromide with these hydrocarbons showed that no chemical compounds are formed. For the system aluminum bromide and benzene, he determined the following crystallization- or solubility-temperatures:

Mol % AlBr	0	3 2	6 8	9 9	13 5	20.4		
Temp. (°C)	5 7	4 5	3.0	1.8	10	20		
Mol % AlBr	29 6	40 4	50.0	58.5	67 1	75 8	85.5	91 9
Temp. (°C)	30	40	50	60	70	80	90	94

The crystallization diagram of these systems consisted of two curves, which cut into each other at a eutectic point at 1.8°. Therefore, aluminum bromide forms no molecular compound with benzene. Since similar observations were made for aluminum bromide with toluene or *p*-xylene, it was obvious that no complexes were formed with these hydrocarbons. However, if moist hydrocarbons were used for the solubility determinations, or if hydrogen bromide was led through the above binary systems, the homogeneous mixture separated into two layers, the lower one containing little aluminum bromide, and the upper one containing much of the salt. Gustavson had assumed this upper layer to be a molecular compound, since its composition corresponded approximately to stoichiometric proportions, and because its aluminum bromide content varied only little with increase of temperature. When Menschutkin led hydrogen bromide through the system $AlBr_3 + C_6H_6$, two layers were formed. The bromine content in these was determined:

upper layer	at 0° 46.81% Br	at 57.5° 47.97% Br
lower layer	at 0° 16.68% Br	at 57.5° 19.88% Br

For the system $AlBr_3 + C_6H_5.CH_3$, the following results were secured:

upper layer	at 0° 44.86% Br	at 75° 46.38% Br
lower layer	at 0° 0.327% Br	at 75° 00.569% Br

From this data Menschutkin assumed that here we have to deal with ternary complexes in which the composition of the liquid varies little with temperature.

[16] G. Gustavson, *J. prakt. Chem.*, 68, 209-234 (1903); *J. Chem. Soc. Abs.*, 84 (I), 804
[17] B. Menschutkin, *J. Russ. Phys.-Chem. Soc.*, 41, 1089-1110 (1909); *C. Z.*, 1910, 1, 167.

The fact that aluminum bromide forms no complexes with benzene, toluene, xylene, naphthalene, and diphenylmethane was also shown by Kablukow and Ssachanow [18] who determined crystallization temperatures of binary systems of these hydrocarbons with aluminum bromide.

Complexes with alkyl halides.—The liquid compounds produced by the action of alkyl halides on aluminum chloride or bromide formed unstable additive products with aromatic hydrocarbons. Thus, by the action of ethyl bromide on aluminum chloride the compound Al_2Cl_6,C_8H_{18} is formed, which combines with 6 moles of benzene to form the additive product $Al_2Cl_6,C_8H_{18},6C_6H_6$. It reacts with ethyl bromide under evolution of hydrogen bromide to yield triethylbenzene.[19] Similarly, from isobutyl chloride and aluminum chloride a compound was obtained which contained 45.9 per cent chlorine.[20] Walker [21] noted considerable conductivity with methyl-, ethyl-, and *n*-propyl iodides as well as ethyl bromide and chloroform solutions of aluminum chloride and assumed the formation of an intermediate compound between the catalyst and the alkyl halide.

The rate of the reaction of benzyl chloride with toluene in the presence of aluminum chloride has been measured by Steele.[22] He found that the reaction is unimolecular and that it comes to a standstill when for every gram equivalent of aluminum chloride, 25 molecules have entered into reaction. Evolution of hydrogen chloride never occurred unless an intense orange color had first developed in the reaction mixture; as the reaction came to an end, the color disappeared almost entirely. The color was assumed to be due to the formation of a complex of the catalyst with benzyl chloride, and cessation of the reaction at a definite point was explained by formation of a complex of aluminum chloride with the hydrocarbon produced.

Wertyporoch and Firla [23] explained the differences in conductivities of several alkyl halide solutions by assuming a primary dehydrohalogenation of such alkyl halides as propyl and isopropyl chloride or chlorocyclohexane to the corresponding olefin, and subsequent formation of highly ionizing olefin-aluminum chloride complexes. Since these complexes were already highly ionized, addition of benzene did not result in as high an increase in conductivity as did addition of the hydrocarbon to an aluminum chloride ethyl chloride complex.

Ternary complexes.—The formation of aluminum chloride complexes as the result of the reaction of alkyl halides with aromatic hydrocarbons has been reported by Gustavson.[24] These were prepared by him in various ways. Thus, by the action of ethyl bromide on aluminum chloride, the compound Al_2Cl_6,C_8H_{10} was formed, and this was combined with

[18] I. Kablukow and A. Ssachanow, *J. Russ. Phys.-Chem. Soc.*, **41**, 1755-1762 (1909); *C. Z.*, **1910**, I, 912.
[19] G. Gustavson, *Compt. rend.*, **136**, 1065-1067 (1903); *J. Chem. Soc. Abs.*, **84** (I), 470 (1903); *J. prakt. Chem. (2)*, **34**, 161-177 (1886); *J. Chem. Soc. Abs.*, **50**, 999 (1886).
[20] G. Gustavson, *J. prakt. Chem. (2)*, **34**, 161-177 (1886).
[21] J. W. Walker, *J. Chem. Soc.*, **85**, 1082-1098 (1904).
[22] B. D. Steele, *J. Chem. Soc.*, **83**, 1470-1490 (1903).
[23] E. Wertyporoch and T. Firla, *Ann.*, **500**, 287-295 (1933).
[24] G. Gustavson, *Compt. rend.*, **136**, 1065-1067 (1903); *J. Chem. Soc. Abs.*, **84** (I), 470 (1903); *J. prakt. Chem. (2)*, **68**, 209-234 (1903); *J. Chem. Soc. Abs.*, **84** (I), 804 (1903).

6 moles of benzene to form the additive product $Al_2Cl_6,C_8H_{16},6C_6H_6$, which is dissociated into its molecular components by heat, and which reacts with ethyl bromide to form a new additive product in which the benzene is replaced by triethylbenzene. Upon heating, the new product decomposes into triethylbenzene and the compound Al_2Cl_6,C_8H_{16}. Triethylbenzene was also produced by reaction of 1 part of aluminum chloride with 1 part of ethyl chloride and 2 parts of benzene. There is first formed an intermediate complex, $Al_2Cl_6,C_6H_3(C_2H_5)_3$, a yellow, viscous liquid, which boils, under partial dissociation, at 135-140°/15 mm, and is decomposed by water to yield triethylbenzene, b. 210-213°.

The only crystalline complexes which Gustavson [25] secured were complexes in which all three components formed ternary molecular compounds; some still contained a molecule of hydrogen chloride. When a current of hydrogen chloride is passed through a mixture of 1 mole of aluminum chloride and 2 moles of *sym*-triethylbenzene, the compound $Al_2Cl_6,2C_6H_3(C_2H_5)_3,HCl$ was formed as a yellow, crystalline mass. The same product was obtained by passing hydrogen chloride through a mixture of $Al_2Cl_6,C_6H_3(C_2H_5)_3$ and *sym*-triethylbenzene at −8°. The compound $Al_2Cl_6,2C_6H_3[CH(CH_3)_2]_3,HCl$ was similarly obtained in the form of yellow crystals. It melted and decomposed at 50° to form triisopropylbenzene. The action of *tert*-butyl chloride and benzene on aluminum chloride at −10° led to formation of a yellow crystalline compound, which was also formed by the action of *p*-di-*tert*-butylbenzene and *tert*-butyl chloride on powdered aluminum chloride at −10°.

Schmidlin and Lang [26] have pointed out that since Menschutkin has shown that aluminum chloride and hydrocarbons do not form molecular compounds, and since those between alkyl halides and aluminum chloride [27] have not been isolated, the only molecular compounds which are formed in Friedel-Crafts alkylations are ternary complexes in which all three components are present.

Schaarschmidt [28] suggests the following scheme for Friedel-Crafts hydrocarbon synthesis:

(1) Activation of the aromatic hydrocarbon by aluminum chloride and a simultaneous "loosening" of the bonds of the organic halogen compound.

(2) Formation of a complex consisting of catalyst, hydrocarbon, and addend in which the aluminum chloride is held by auxiliary valences and the addend by ordinary valences, thus:

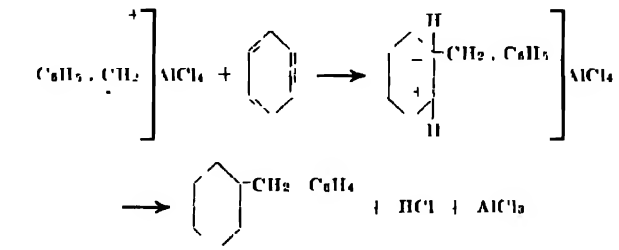
$$\begin{matrix} & & R' \\ & & | \\ Cl_3Al & ::: & C_6H_5 \end{matrix}$$

[25] C. Gustavson *J. prakt. Chem.* (2), **72**, 57-79 (1905); *J. Chem. Soc. Abs.*, **88** (I), 696 (1905); *Compt. rend.*, **140**, 940-941 (1905); *J. Chem. Soc., Abs.*, **88** (I), 334 (1905).
[26] J. Schmidlin and R. Lang, *Ber.*, **45**, 809-912 (1912).
[27] B. D. Steele *J. Chem. Soc.*, **83**, 1470-1490 (1903).
[28] A. Schaarschmidt, *Z. angew. Chem.*, **37**, 286-288 (1924); *C. A.*, **18**, 2874.

This complex involves the formation of a partially saturated benzene.

(3) The stability of this complex depends upon the division of inner valences. In alkylation, splitting is assumed to occur at the point where addition has taken place to involve ordinary valences. The metallic chloride and the double bond is thereby regenerated, so that stoichiometric quantities of it are not required.

The formation of a benzyl chloride-aluminum chloride complex has been more recently advanced by Dilthey,[29] who suggests the following scheme for its reaction with benzene:



Here, too, there is postulated an intermediate formation of a dihydrobenzene derivative.

Physico-chemical studies.—Conductivity measurements of solutions of aluminum bromide in ethyl bromide in the presence of benzene and other hydrocarbons which have been made by Wertyporoch and his co-workers [30] point to the formation of ionized complex ternary products in the Friedel-Crafts reaction. The investigation was at first conducted only with aluminum bromide in ethyl bromide because of the better solubility of aluminum bromide; subsequently, however, a series of investigations was made with aluminum chloride in ethyl, propyl, isopropyl, and cyclohexyl halides.[31] The purified alkyl halides used showed practically no specific conductivity; addition of aluminum chloride to ethyl chloride resulted in slightly increased conductivity, which was practically constant for 0.025 to 0.2 mole of aluminum chloride. This was explained by assuming that the auto-complex, Al_2Cl_6 or Al_4Cl_{12}, which through solvate formation may be changed into $Al(C_2H_5Cl)_nAlCl_3$ or $Al(C_2H_5Cl)_n(AlCl_4)_3$, binds ethyl chloride in the cation. Dilution does not result in noticeable decomposition, although in very small concentrations it does become completely dissociated.

With propyl, isopropyl, and cyclohexyl chlorides, molar conductivity upon addition of aluminum chloride is about thirty times as great. This was explained by assuming dehydrohalogenation of the alkyl halide and the formation of an aluminum chloride complex with the resulting olefin.

[29] W. Dilthey, *Ber.*, **71**, 1350-1353 (1938).
[30] A. Wohl and E. Wertyporoch, *Ber.*, **64**, 1357-1369 (1931). E. Wertyporoch, *Ber.*, **64**, 1369-1380 (1931).
[31] E. Wertyporoch and T. Fuła, *Z. physik. Chem.*, **A162**, 398-414 (1932); *Ann.*, **500**, 287-295 (1933)

Conductivity, change in color, and hydrogen chloride cleavage increase with aluminum chloride concentration.

In all cases, addition of benzene to the complexes results in formation of the correspondingly alkylated compounds and increase in the conductivity. This is greatest with ethyl chloride, which is bound to the aluminum chloride only as a pseudosalt; here conductivity is 108 times as great as it was for the solution of aluminum chloride in ethyl chloride. In the other cases in which more stable complexes had been formed, conductivity upon addition of benzene is increased less than two-fold. Ionized ternary complexes are assumed to be formed; in these there is hypothesized a loosening of the bond between halogen and carbon of the halide component and a loosening of hydrogen in the benzene nucleus Stabilization occurs upon formation of alkyl benzene.

Addition of cyclohexane to a 2.7 per cent solution of aluminum chloride in chlorocyclohexane resulted in no increase in conductivity. The use of hydrogenated aromatic hydrocarbons in the Friedel-Crafts reaction obviously requires a much greater concentration of aluminum chloride.

In a later study [32] the conductivity of aluminum chloride solutions in butyl, isobutyl, amyl, isoamyl, and hexyl chlorides was investigated. Molar conductivity was found to increase with the concentration Unsaturated hydrocarbons were formed by cleavage of hydrogen chloride, and these were assumed to form complexes with the catalyst.

In kinetic studies, Ulich and Heyne [33] have found evidence of the formation of a complex between the catalyst and propyl chloride. The complex MCl_3,C_3H_7Cl reaches an equilibrium with the metal halide, benzene, and the product. The rate of the alkylation was directly proportional to concentration of MCl_3,C_3H_7Cl and of the hydrocarbon, which according to Price and Ciskowski [34] indicates that any further function of the catalyst in activating the hydrocarbon is negligible. Ulich and Heyne note that results with propyl chloride fit fairly well the expression:

$$dv/dt = K'(GaCl_3,C_3H_7Cl)(C_6H_6) = k(GaCl_3)(C_3H_7Cl)(C_6H_6)/(C_6H_6) + K(C_3H_7Cl)$$

in which $k = 750$ and $K = 0.5$. With aluminum chloride instead of gallium chloride as catalyst, there is only partial agreement with this mechanism, since here reaction primarily occurs by complex formation with the product.

Polynuclear Hydrocarbons and Unsubstituted, Saturated Alkyl Halides

Since the action of aluminum chloride on naphthalene results in condensation and decomposition, Friedel-Crafts alkylation of naphthalene is successful only under very mild conditions. Attempts to methylate naph-

[32] E. Wertyporoch and I Kowalski *Z. physik. Chem.*, **A166**, 205-218 (1933); *C. A.*, **28**, 397.
[33] H. Ulich and G. Heyne, *Z. Elektrochem.*, **41**, 509-514 (1935); *C A*, **29**, 7768
[34] C. C. Price and J M Ciskowski, *J Am. Chem. Soc*, **60**, 2499-2502 (1938).

thalene were at first unsuccessful.[97] Recently it has been possible to secure very small yields of methylated naphthalenes at ordinary temperatures. With methyl iodide, a 5 per cent yield of a mixture of α- and β-methylnaphthalene, in which the α-compound predominated, was obtained.[98] With methyl bromide, an 8 per cent mixture of equal parts of α- and β-methylnaphthalenes was secured. The best yield was obtained using methyl chloride, 10.7 per cent of only the β-compound being obtained in almost pure form.

Under careful warming, so as not to decompose the naphthalene, β-ethylnaphthalene has been prepared by reaction with ethyl bromide.[99] Binaphthyl was also formed. Reaction of naphthalene with ethyl iodide was shown to result in the formation of β-ethylnaphthalene together with a very small amount of the α-compound.[100] With 100 parts of naphthalene, 50 parts of ethyl chloride, and 15 parts of aluminum chloride, β-ethylnaphthalene has been prepared.[101]

From a hot mixture of 350 g of naphthalene and 200 g of *n*-propyl bromide, β-isopropylnaphthalene in an almost pure state has been obtained.[102] Here about the same proportion of reactants were used as in the preparation of β-methylnaphthalene noted above.

An excess of naphthalene has also been used in the preparation of *tert*-butylnaphthalene from 15 parts of naphthalene, 6 parts of isobutyl bromide, and 1 part of aluminum chloride.[103] The reaction was effected at 100°. β,β-dinaphthyl has also been reported to be a product of the reaction.[104] Gump [105] heated 2 moles of *tert*-butyl chloride with 1 mole of naphthalene in the presence of a small amount of aluminum chloride and obtained a mixture of two di-*tert*-butylnaphthalenes, one boiling at 319° and melting at 82-83°, and the other boiling at 320° and melting at 145-146°. The two were separated by fractional crystallization from alcohol. Gump suggests that these are probably identical with the "dinaphthyls" reported to be formed in the reaction between isobutyl chloride and naphthalene. Gump could not prepare a *tert*-butylnaphthalene from equimolecular amounts of the reactants.

Using an excess of naphthalene, β-amylnaphthalene is secured by treatment of naphthalene with amyl chloride (obtained from isobutyl carbinol) in the presence of a small amount of aluminum chloride.[102] Chlorination of paraffin material containing 8 to 20 carbon atoms to an extent sufficient to produce a mixture of the corresponding alkyl monochloride, without the production of any substantial quantity of alkyl polychlorides, and subsequent treatment of the resulting mixture of alkyl

[97] L. Roux, *Ann. chim. phys.*, 12, 289-358 (1887), *J. Chem. Soc. Abs.*, 54, 1305 (1888). C. A. Bischoff, *Ber.*, 23, 1905-1908 (1890); *J. Chem. Soc. Abs.*, 58 (II), 1145 (1890). O. Brunel, *Ber.*, 17, 1179-1180 (1884).

[98] Tcheoulaki and Yung Fu, *Contrib. Inst. Chem., Nat. Acad. Peiping*, 2, 127-145 (1936); *Chem. Zentr.*, 1937, II, 2523.

[99] O. Brunel, *Ber.*, 17, 1179-1180 (1884).

[100] L. Roux, *Ann. chim. phys. (6)*, 12, 307 (1887).

[101] C. Marchetti, *Gazz. Chim. ital.*, 11, 265, 439 (1881)

[102] L. Roux, *loc. cit.* L. Roux, *Bull. soc. chim.*, 41, 379-382; *J. Chem. Soc. Abs.*, 1357 (1888).

[103] A. Baur, *Ber.*, 27, 1623 (1894).

[104] R. Wegscheider, *Monatsh.*, 5, 237 (1884).

[105] W. Gump., *J. Am. Chem. Soc.*, 53, 380-381 (1931); *Brit. Chem. Abstracts-A.* 341 (1931).

chloride and paraffin hydrocarbon with naphthalene in the presence of aluminum chloride results in a mixture of alkylated naphthalene and uncondensed material easily separated by distillation.[106]

Higher alkylated naphthalenes may be made water-soluble by, *e.g.*, sulfonation, and find use as detergents, wetting and tanning agents, foaming compounds, etc. An alkylated naphthalene, produced by reaction with, for example, *tert*-butyl chloride in the presence of aluminum chloride, is sulfonated for the preparation of a wetting agent.[107] Sodium diisopropylnaphthalene sulfonate and sodium tetradecylnaphthalene sulfonate may be employed in the preparation of a dry-cleaning agent, according to a patent recently granted to National Aniline and Chemical Company.[108] Propyl-, isopropyl-, butyl- and isobutylnaphthalenes may be sulfonated and used with pyrophosphates as washing agents.[109] Compounds of 8 to 20 carbon atoms produced by polymerization of olefins are chlorinated, and the resulting alkyl chlorides are condensed with naphthalene. The sulfonation products of these higher alkylated naphthalenes are claimed as wetting, emulsifying, and washing agents.[110]

Table 6. Alkylation of Naphthalene

Compound Formed	Alkyl Halide	Reference
no Methylnaphthalene	methyl chloride	1, 6, 7
β-Methylnaphthalene	methyl chloride	2
β-Methylnaphthalene	methyl bromide	2
β-Methylnaphthalene	methyl iodide	3
α-Methylnaphthalene	methyl bromide	2
α-Methylnaphthalene	methyl iodide	3
β-Ethylnaphthalene	ethyl chloride	8
β-Ethylnaphthalene	ethyl bromide	7
β-Ethylnaphthalene	ethyl iodide	9
α-Ethylnaphthalene	ethyl iodide	9
β-Isapropylnaphthalene	*n*-propyl bromide	1
tert(?)Butylnaphthalene	isobutyl chloride	5
tert(?)Butylnaphthalene	isobutyl bromide	4
Di-*tert*-butylnaphthalene	*tert*-butyl chloride	10
β-Isoamylnaphthalene	isoamyl chloride	1

References

1. L. Roux, *Ann. chim. phys.*, 12, 289-358 (1887); *J. Chem Soc. Abs.*, 54, 1305 (1888)
2. Techeoufaki and Yung Fu, *Contr. Inst. Chem., Natl. Acad. Peiping*, 2, 149-166 (1936), *C. Z.*, 1937, II, 2523.
3. Techeoufaki and Yung Fu, *Contr. Inst. Chem., Natl. Acad. Peiping*, 2, 127-145 (1936) *C. Z.*, 1937, II, 2523.
4. A. Baur, *Ber.*, 27, 1623 (1894).
5. R. Wegscheider, *Monatsh.*, 5, 237 (1884)
6. C. A. Bischoff, *Ber.*, 23, 1905-8 (1890); *J. Chem. Soc. Abs.*, 58 (II) 1145 (1890)
7. O. Brunel, *Ber.*, 17, 1179-1180 (1884).
8. C. Marchetti, *Gazz. chim. ital.*, 11, 265 439 (1881).
9. L. Roux, *Ann. chim. phys. (6)*, 12, 307 (1887).
10. W. Gunip, *J. Am. Chem. Soc.*, 53, 380-381 (1931), *Brit. Chem. Abstracts-A*, 341 (1931)

Mineral oil fractions containing more than eight carbon atoms may be chlorinated and condensed with naphthalene or with methylated naphthalenes. The sulfonated alkylnaphthalenes are claimed as wetting and cleansing agents.[111] Thus 380 parts (by weight) of a chlorinated light-

[106] U. S. P. 2,072,061 (1937) to C. A. Thomas (to Sharples Solvents Corp.). *C. A.*, 31, 2613.
[107] U. S. P. 1,980,543 (1934) to Eli Lurie. *C. A.*, 29, 258 (1935).
[108] Canadian P. 369,508 to L. H. Flett (to National Aniline and Chemical Co.) (1937).
[109] British P. 447,072 to W. J. Tennant
[110] U. S. P. 1,992,160 (1935) to C. A. Thomas (to Sharples Solvents Corp.).
[111] British P. 416,379 (1934) to I. G. Farbenindustrie

petroleum fraction is caused to react with 10 parts by weight of aluminum chloride in 250 parts of naphthalene at 90°, and the product is subsequently sulfonated.[112]

The Friedel-Crafts reaction with tetralin results exclusively in substitution in the β-position. With aluminum bromide instead of aluminum chloride, the yields can be so increased as to make the reaction serviceable.[113] The action of the two catalysts has been contrasted in the preparation of alkyl derivatives of tetralin:

Catalyst	Derivative	% Yield
$AlBr_3$	β-ethyl-	28
$AlCl_3$	β-ethyl-	2.5
$AlBr_3$	β-isopropyl-	70
$AlCl_3$	β-isopropyl-	24.5

It is claimed that biphenyl and *n*-propyl or isopropyl chloride react rapidly at 90-95° in the presence of aluminum chloride to give isopropyl biphenyls.[114]

The action of ethyl bromide on acenaphthene in the presence of aluminum chloride results in the formation of 5-ethylacenaphthene, b.p. 166°/20 mm, and 310°/760 mm.[115]

The alkylation of polynuclear hydrocarbons (of at least three benzene rings) has been effected by carrying out the reaction under pressure Thus pyrene or chrysene may be heated with an aliphatic halide of at least 8 carbon atoms to give, *e.g.*, polyoctylpyrene or chrysene. The products have been claimed to impart fluorescence to oils, fats, and waxes.[116]

Condensation of aromatic hydrocarbons having at least 4 condensed nuclei with aliphatic or cycloaliphatic hydrocarbons containing halogen, (*e.g.*, alkyl halides of at least 7 carbon atoms), in the presence of aluminum chloride gives products which impart a vivid and powerful fluorescence to mineral oils.[117]

Reactions of Tri-alkylated Chloromethanes with Benzene

The reaction of alkyl-substituted chloromethanes with benzene in the presence of aluminum chloride results in evolution of hydrogen chloride and the formation of the corresponding phenyl compound. The following compounds have been prepared by the action of benzene and aluminum chloride on the indicated chloro-alkyl-methanes :[118]

Chloromethane Derivative	Phenylmethane Derivative Formed	b.p.
Dimethyl-*n*-propyl-	dimethyl-*n*-propyl-	205-6°
Dimethylisobutyl-	dimethylisobutyl-	218°
Methyldiethyl-	methyldiethyl-	204-6°
Triethyl-	triethyl-	220-222°

[112] German P. 647,988 (1937) to I. G. Farbenindustrie.
[113] A. Barbot, *Bull. soc. chim. (4)*, **47**, 1314-1323 (1930); *C. A.*, **25**, 043.
[114] British P. 497,284 (1939) to E. I. du Pont; *C. Z.*, 1939, I, 3961
[115] F. Mayer and W. Kaufmann, *Ber.*, **53**, 289-298 (1920); *J. Chem. Soc. Abs.*, **118** (I), 301 (1920).
[116] French P. 818 185 (1938) to I. G. Farbenindustrie; *C. A.*, **32**, 2146.
[117] British P. 473,653 (1938) to I. G. Farbenindustrie; *Brit. Chem. Abstracts*-B, 30 (1938).
[118] E. Schreiner, *J. prakt. Chem.*, **82**, 292-296 (1910); *C. Z.*, 1910, II, 1133.

Halse [119] reported that this Friedel-Crafts reaction ran smoothly in numerous preparations performed by him The reaction, however, was found to be reversible:

$$C_6H_4R_2 + C_6H_6 \rightleftharpoons 2C_6H_5R$$

Much aluminum-chloride and little benzene was found to reverse the reaction, and *vice versa*. By the use of the corresponding alkyl chloromethane with benzene and aluminum chloride, the following compounds were secured:

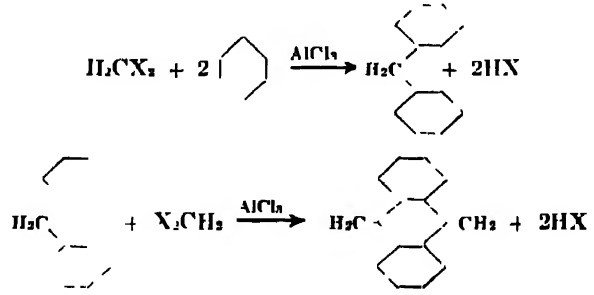
Phenylmethane Derivative Formed	b p.
methylethyl-*n*-propyl-	110-112°/15 mm
methyl-di-*n*-propyl-	120-121°/12 mm
diethyl-*n*-propyl-	237-238°
dimethylisoamyl-	116-117°/14 mm
methylethylisoamyl-	122-123°/14 mm
ethyldi-*n*-propyl-	127-128°/15 mm
diethylisobutyl-	240-242°
methyldiisobutyl-	143-144°/18 mm
tri-*n*-propyl-	140-141°/15 mm
isobutyldi-*n*-propyl-	143-144°/11 mm
methyldiisoamyl-	153-155°/15 mm
ethyldiisoamyl-	170-172°/14 mm
n-propyldiisoamyl-	180-181°/15 mm
isobutyldiisoamyl-	172-173°/11 mm

It is to be noted that during the above reactions, no further branching of the alkyl halide occurred.

Reaction of Di- and Polyhalogenated Saturated Aliphatic Hydrocarbons with Aromatic Hydrocarbons

Dihalides

Friedel-Crafts reaction of saturated dichlorinated aliphatic hydrocarbons proceeds not only with substitution of both chlorine atoms, but also by subsequent reaction of the initial product with more of the halogenated component, so that polynuclear compounds are also formed in the reaction. With dihalogenated methanes, for example, the reaction is:



During the last reaction the hydroanthracene is probably reduced to anthracene and methyl halide, however; and the alkyl halide formed

[119] O. M. Halse, *J. prakt. Chem. (2)*, **89**, 451-465 (1914); *C. Z.*, 1914, II, 23-25.

reacts with the benzene present. The final reaction products are, therefore, diphenylmethane, anthracene, and toluene.[120] The relative quantities of diphenylmethane and anthracene which are obtained depend on the proportions of dichloromethane and benzene used.

Toluene and dichloromethane in the presence of aluminum chloride similarly yield[121] a mixture of *m*- and *p*-xylene, boiling at 130-150°, ditolyl methane, boiling at 280-290°, and dimethylanthracene. It has been shown[122] that this "dimethylanthracene" is a mixture of three isomeric dimethylanthracenes, melting at 240°, 244.5°, and 86°, respectively, and of β-monomethylanthracene, and that in addition to these anthracene derivatives there are also formed di-*m*-tolylmethane, di-*p*-tolylmethane, benzene, and xylene. The course of the reaction appeared to be:

(1) The formation of ditolylmethane derivatives by the direct action of toluene and dichloromethane.
(2) The interaction of the ditolylmethanes with a second molecule of dichloromethane to form a hydride of dimethylanthracene, which reacts with a third molecule of dichloromethane to form methyl chloride and the corresponding anthracene derivative.
(3) The methyl chloride thus formed reacts with toluene to yield xylene.
(4) The benzene is formed from toluene by action of the aluminum chloride.
(5) The β-monomethylanthracene is the product of the reaction of benzene and toluene with dichloromethane.

Details of the separation of the three dimethylanthracenes obtained were communicated by Lavaux.[123] He found that the two dimethylanthracenes, melting at 240° and 244.5°, formed a eutectic mixture having a melting point of 225°. The compound, m. 240°, was thought to be 1,6-, and that m. 244.5°, 2,7-dimethylanthracene.

In order to solve the problem of the constitution of the supposed 1,6- and 2,7-dimethylanthracenes obtained by the action of dichloromethane and aluminum chloride on a mixture of isomeric ditolylmethanes, the condensation was repeated, using a pure specimen of di-*p*-tolylmethane.[124] It was found, however, that the pure hydrocarbon gave the same mixture of dimethylanthracenes, indicating that aluminum chloride had brought about a transposition similar to that which it effects in converting *n*-propyl into isopropyl derivatives.

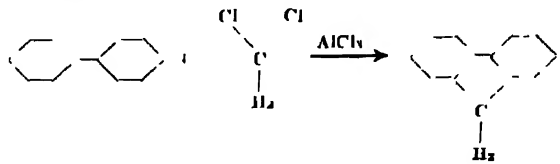
The ratio of ditolylmethane to dimethylanthracenes formed is 20:1.[125] Other alkylated benzenes have been reacted with dichloromethane and aluminum chloride.[126] With *m*-xylene there is obtained, in addition to

[120] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 11, 263-277; *J. Chem. Soc. Abs.*, 52, 1102 (1887).
[121] C. Friedel and J. M. Crafts, *loc. cit.*; *Bull. soc. chim. (2)*, 41, 322-327 (1884); *J. Chem. Soc. Abs.*, 1312 (1884).
[122] J. Lavaux, *Compt. rend.*, 139, 976-978 (1904); *J. Chem. Soc. Abs.* (I), 43 (1905).
[123] J. Lavaux, *Compt. rend.*, 140, 44-45 (1905); *J. Chem. Soc. Abs.* (I), 125 (1905).
[124] J. Lavaux, *Compt. rend.*, 152, 1400-1402 (1911); *J. Chem. Soc. Abs.*, 100 (I), 533 (1911).
[125] J. Lavaux and M. Lombard, *Bull. soc. chim.*, 7, 913-915 (4) (1910); *J. Chem. Soc. Abs.*, 98 (I), 747 (1910).
[126] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 11, 263-277 (1887); *J. Chem. Soc. Abs.*, 52, 1102 (1887).

liquid products, a tetramethylanthracene, m.p. 162-163°. Pseudocumene was found to yield durene, a small quantity of tetramethylanthracene identical with that obtained from *m*-xylene, a hexamethylanthracene, m.p. 220°, and hepta- or octa-methylanthracene, m.p. 290°.

Reacting mesitylene with dibromomethane in the presence of aluminum chloride, dimesitylmethane, m.p. 135°, is prepared.[127] The reaction with pseudocumene proceeds with much greater difficulty, di-pseudocumylmethane, b.p. 189-190°/12 mm and m.p. 99°, being obtained only in small yield.[128] This was not identified by Friedel and Crafts[126] as one of the products of the reaction of pseudocumene and dichloromethane.

An interesting reaction is the production of fluorene from dichloromethane and biphenyl:



The condensation is effected by adding 10 parts of dichloromethane to a mixture comprising 15 parts of biphenyl and 1 part of aluminum chloride.[129]

The principal products of the action of dichloromethane on naphthalene with aluminum chloride are β-methylnaphthalene and β,β-binaphthyl. Full details of the separation and identification of these products have been given.[130]

In the Friedel-Crafts reaction of dichloromethane with naphthalene the only product is β,β-binaphthyl if the initial stage of the reaction is not effected at the ordinary temperature and if the distillation of the products of the reaction is not carried out under diminished pressure.[131]

By the action of anhydrous aluminum chloride on benzene and ethylene dichloride, there is obtained a crude product, which was separated into two fractions, one boiling at 80-280°, and the other above 280°. The former contains small amounts of ethylbenzene; in the latter is a fraction boiling above 340°, which may be triphenylethane.[132] Diphenylethane, m.p. 52.5° and b.p. 276-277°, is also one of the products.[133] With ethylene dibromide and toluene in the presence of aluminum chloride, ditolylethane, $C_2H_4(C_6H_4.CH_3)_2$, b.p. 297-300°, has been secured.[134] Similarly, dimesitylethane, m.p. 117-118°, is obtained from mesitylene and ethylene dibromide.[135]

The action of ethylene dibromide on naphthalene with aluminum

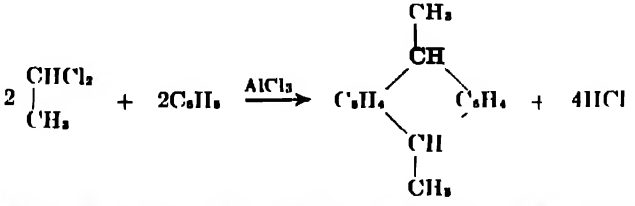
[127] F. Wenzel and R. Kugel, *Monatsh.*, 35, 953-963 (1914); *J. Chem. Soc. Abs.*, 108 (I), 514 (1915)
[128] F. Wenzel and G. Drada, *Monatsh.*, 35, 973-986 (1914); *J. Chem. Soc. Abs.*, 108 (I), 514 (1915).
[129] P. Adam, *Compt. rend.*, 103, 207-208 (1886); *J. Chem. Soc. Abs.*, 50, 1033
[130] F. Bodroux, *Bull. soc. chim. (3)* 25, 491-497 (1901); *J. Chem. Soc. Abs.*, 80 (I), 374 (1901)
[131] A. Homer, *J. Chem. Soc.*, 97, 1141-1154 (1910)
[132] R. D. Silva, *Bull. soc. chim. (2)*, 36, 24-26 (1881); *J. Chem. Soc. Abs.*, 913 (1881)
[133] R. D. Silva, *Compt. rend.*, 89, 606-608 (1879); *J. Chem. Soc. Abs.*, 259 (1880)
[134] C. Friedel and M. Balsohn, *Bull. soc. chim.*, 35, 52-54 (1881); *J. Chem. Soc. Abs.*, 260 (1881)
[135] F. Wenzel and R. Kugel, *Monatsh.*, 35, 953-963 (1914); *J. Chem. Soc. Abs.*, 108 (I), 514 (1915).

chloride yields picene as a result of a secondary reaction, namely the decomposition of the *sym*-dinaphthylethane, $C_2H_4(C_{10}H_7)_2$, first formed. Conditions for the easy preparation of pure picene by means of the Friedel-Crafts synthesis with ethylene bromide have been given.[131]

Aliphatic compounds of relatively short chain containing two halogen groups, *e.g.*, dichloromethane, ethylene dichloride, or similar products obtained from heavier aliphatic hydrocarbons up to about 5 carbon atoms, may be condensed with aromatics or hydroaromatics in the presence of aluminum chloride to give addition products of high molecular weight which, according to the reaction time, are oily liquids or soluble plastic resins. For example, when a mixture of 200 parts by weight of benzene, 255 parts of ethylene dichloride, and 40 parts of aluminum chloride is heated at 40° for about four hours, a homogeneous oily material is obtained which, when distilled to 250° at 1 mm, yields a relatively large quantity of a distillate rich in diphenylethane. The residue consists of 77 parts by weight of an oily material, having a molecular weight below 1000. By increasing the time of polymerization, a product of higher molecular weight is obtained. These polymers, or their alkylation products with, *e.g.*, amyl chloride, have been claimed as blending agents for oils and lubricants.[136]

Elastic plastic materials which are very resistant to the action of many solvents and chemical reagents may be prepared by reacting an ethylene dihalide in the presence of aluminum chloride with an aromatic hydrocarbon having the general formula, RC_6H_4R, where R and R each represent hydrogen or a saturated aliphatic hydrocarbon radical containing more than one carbon atom. The properties of the plastic (AXF) make it especially interesting as a compounding ingredient for natural or synthetic rubber.[137]

Reacting ethylidene chloride with benzene and aluminum chloride, the formation of *asym*-diphenylethane has been reported.[138] Besides this liquid product, a solid, 9,10-dihydro-9,10-dimethylanthracene has been obtained.[139] Experimental proof that this compound was the hydride, and not dimethylanthracene, has been offered,[140] and the following equation for the formation of the hydride, m.p. 181-181.5°, from benzene and ethylidene chloride or bromide has been proposed:



[136] U. S. P. 2,072,107 (1937) to Fulton and Mikeska (to Standard Oil Development Co.)
[137] S. D. Shunkle, A. E. Brooks, and G. H. Cady, *Ind. Eng. Chem.*, **28**, 275-280 (1936). U. S. P. 2,016,026-7 (1935) to S. D. Shunkle.
[138] R. D. Silva, *Bull. soc. chim. (2)*, **41**, 448-449 (1884); *J. Chem. Soc. Abs.*, 1356 (1884). *Compt. rend.*, **99**, 606-608 (1879); *J. Chem. Soc. Abs.*, 259 (1880).
[139] A. Angeblis and R. Anschütz, *Ber.*, **17**, 165-167 (1884); *J. Chem. Soc. Abs.*, 753 (1884).
[140] R. Anschütz and E. Romig, *Ber.*, **18**, 662-666 (1885); *J. Chem. Soc. Abs.*, **48**, 768 (1885). R. Anschütz, *Ann.*, **235**, 302-327 (1886).

Besides the *asym*-diphenylethane already mentioned, ethylbenzene also has been found to be a product of the reaction.

The action of ethylidene chloride on toluene and on *m*-xylene has been investigated[140] Reacting 30 g of ethylidene chloride with 180 g of toluene and 15-20 g of aluminum chloride, the following products have been obtained:

p-ethyltoluene, b.p. 160-163°.
asym-*p*-ditolylethane, b p. 295-298°. (The main product of the reaction; from 30 g of ethylidene chloride, 17-20 g of ditolylethane was obtained.)
β,β'-dimethyl-mesodimethylanthracenehydride, m.p. 170.5-171°.

The formation of the ditolylethane can be expressed by the equation:

$$CH_3CHCl_2 + 2C_6H_5\ CH_3 \longrightarrow \begin{matrix} CH_3 . C_6H_4 \diagdown \\ \qquad\qquad CH . CH_3 \\ CH_3\ C_6H_4 \diagup \end{matrix} + 2HCl$$

The tetramethylanthracenehydride is formed as follows:

$$2CH_3 . CHCl_2 + 2C_6H_5\ CH_3 \longrightarrow CH_3\ C_6H_4 \begin{matrix} CH_3 \\ | \\ CH \\ \diagup \\ \diagdown \\ CH \\ | \\ CH_3 \end{matrix} C_6H_4\ CH_3 + 4HCl$$

Reacting ethylidene chloride in the same way with *m*-xylene and aluminum chloride, no anthracene derivative is obtained; there have been secured, however, the expected ethyl-*m*-xylene, b p. 186-187°, and dixylylethane, b.p. 323-325°, b_{11} 169-172°.

The various hydrocarbons obtained by the action of ethylidene chloride on benzene, toluene, and *m*-xylene in the presence of aluminum chloride are summarized:

Hydrocarbon Used	Reaction Products: Benzene Series	Diphenylethane Series	Anthracene Series
Benzene	ethylbenzene	*asym*-diphenylethane	dimethylanthracene-hydride
Toluene	1 4-ethyltoluene	*asym*-ditolylethane	tetramethylanthracene-hydride
Xylene	1 3,4-ethylxylene	*asym*-dixylylethane	

The ditolylethane obtained from toluene and ethylidene chloride has been identified as 1,1-di-*p*-tolylethane Assuming that the tetramethylanthracenedihydride obtained in the same reaction was produced by the further action of 1 mole of ethylidene chloride on 1 mole of this di-*p*-tolylethane, then it can only be 2,7,9,10-tetramethylanthracenedihydride.[141]

[141] J. Lavaux, *Compt rend* 141, 354-356 (1905), *J Chem Soc Abs*, 88 (I), 698 (1905).

The action of ethylidene chloride on naphthalene in the presence of aluminum chloride results in the production of β-methylnaphthalene together with small quantities of α-methylnaphthalene, α- and β-ethylnaphthalenes, dimethylnaphthalenes, and β,β-binaphthyl; a large quantity of methane is evolved.[142] If the initial stage of the reaction is allowed to proceed at the ordinary temperature, and if the distillation of the products of the reaction is carried out at reduced pressure, the action of *asym*-dichloroethane on naphthalene yields β-dinaphthylmethane.[143]

Propylene chloride (1,2-dichloropropane) and benzene in the presence of aluminum chloride yield 1,2-diphenylpropane, b.p. 277-279°.[144] 1,3-diphenylpropane and propylbenzene have been secured by heating at 60° a mixture of benzene, aluminum chloride, and 1,3-dibromopropane.[145] With isobutylene dibromide are formed 1-phenyl-2-methylpropane, $CH_2.C_6H_5.CH(CH_3)_2$, 1,2-diphenyl-2-methylpropane, $CH_2C_6H_5.C(CH_3)_2.C_6H_5$, and a small amount of a substance melting at 128° upon crystallizing from alcohol.[146]

By the action of *m*-xylene on 2,2-dichloropropane, or on a mixture of 2,2-dichloropropane and 2-chloropropylene, a 25-27 per cent yield of 2,2-di-*m*-xylylpropane, m.p. 174.5°, has been secured.[147] Attempts to prepare dimesitylpropane from trimethylene dibromide and mesitylene with aluminum chloride have been unsuccessful.[148]

By gradual addition of 8 g of aluminum chloride to a mixture of 200 g of benzene and 50 g of 1,1-dichloroheptane, disubstitution occurs with formation of α,α-diphenylheptane.[149] When the proportion of catalyst is much greater, however, the product is *n*-heptylbenzene, possibly because of cleavage of primarily formed diphenylheptane.

Di-tertiary 1,4-dichlorides add to aromatic hydrocarbons to form new ring systems, 2,5-dichloro-2,5-dimethylhexane with benzene and aluminum chloride yielding 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene.[150]

Trihalides

The reaction of polychloroalkyls with aromatic compounds in the presence of aluminum chloride has been most used for the preparation of tri- and tetra-phenyl substituted methanes. In 1877 Friedel and Crafts [151] reported that chloroform and carbon tetrachloride reacted easily in the cold with benzene to yield triphenyl- and tetraphenylmethane, respectively:

[142] F. Bodroux, *Bull. soc. chim. (3)*, **25**, 491-497 (1901); *J. Chem. Soc. Abs.*, **80** (I), 374 (1901).
[143] A. Homes, *J. Chem. Soc.*, **97**, 1141 (1910).
[144] R. D. Silva, *Compt. rend.*, **89**, 606-608 (1879); *J. Chem. Soc. Abs.*, 259 (1880); *Jahresber. über die Fortschritte der Chemie*, 379-380 (1879).
[145] F. Bodroux, *Compt. rend.*, **132**, 155-157 (1901); *J. Chem. Soc. Abs.*, **80** (I), 196 (1901). For reaction of 1,3-chlorobromopropane with benzene, see I. Tsukervanik and K. Yanurskii, *J. Gen. Chem. (U.S.S.R.)*, **10**, 1075-6 (1940).
[146] F. Bodroux, *Compt. rend.*, **132**, 1333-1336 (1901); *J. Chem. Soc. Abs.*, **80** (I), 523 (1901).
[147] H. Goudet and F. Schenker, *Helv. chim. Acta*, **10**, 132-140 (1927); *Brit. Chem. Abstracts-A*, 440 (1927).
[148] F. Wenzel and R. Kugel, *Monatsh.*, **35**, 953-963 (1914); *J. Chem. Soc., Abs.*, **108** (I), 514 (1915).
[149] V. Auger, *Bull. soc. chim. (3)*, **47**, 49 (1887); *cf.* F. Krafft, *Ber.*, **19**, 2982-2988 (1886).
[150] H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, **62**, 36-44 (1940); see also p. 432.
[151] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2)*, **28**, 50 (1877).

$$CHCl_3 + 3C_6H_6 \longrightarrow CH(C_6H_5)_3 + 3HCl$$

and

$$CCl_4 + 4C_6H_6 \longrightarrow C(C_6H_5)_4 + 4HCl$$

A few years later Schwarz [152] described the reaction of benzene and chloroform, saying that tetraphenylethylene was also obtained. Emil and Otto Fischer [153] utilized the reaction in the preparation of dyes of the triphenylmethane series They found that diphenylmethane was also produced in considerable quantity, and attributed its formation to reduction of an intermediate product, diphenylchloromethane, by the aluminum chloride.

Friedel and Crafts [154] reattacked the problem. They obtained the best yield of triphenylmethane by mixing 1000 g of benzene and 200 g of chloroform, and adding to the mixture 200 g of aluminum chloride in four or five portions. The whole was kept at the boiling point of benzene for two hours. Only 130 g of hydrogen chloride were evolved instead of 183.4 g, as required by the equation:

$$CHCl_3 + 3C_6H_6 \longrightarrow CH(C_6H_5)_3 + 3HCl$$

The authors suggested that Fischer's theory of the formation of diphenylmethane required the evolution of all the hydrogen chloride That portion of the distillate boiling above 150° weighed 280 g On heating to 200° it gave off hydrogen chloride and yielded on fractionation 40 g of diphenylmethane, 150 g of triphenylmethane, and 50 g of carbonaceous residue and other substances of higher boiling points than triphenylmethane. When the crude product is heated to 200° there is possibly a reaction of the chloride, $CHCl(C_6H_5)_2$, and the triphenylmethane, with formation of diphenylmethane. For that reason, it was recommended that prolonged heating should be avoided in the preparation of triphenylmethane.

According to Böeseken,[155] when 45 g of chloroform is gradually added to an excess of benzene containing aluminum chloride, a mixture of 6 g of diphenylmethane, 11.6 g of triphenylmethane, and 24.1 g of triphenylchloromethane is formed. Böeseken suggests that the following probably occurs in the action of chloroform with benzene:

(1) $CHCl_3.AlCl_3 + C_6H_6 \longrightarrow CHC_6H_5Cl_2.AlCl_3$

(2) $CHC_6H_5Cl_2.AlCl_3 + C_6H_6 \longrightarrow CH(C_6H_5)_2Cl, AlCl_3$

(3) $CH(C_6H_5)_2Cl.AlCl_3 + C_6H_6 \longrightarrow CH(C_6H_5)_3$

The diphenylchloromethane may decompose thus:

$$2CH(C_6H_5)_2Cl \longrightarrow CH_2(C_6H_5)_2 + C(C_6H_5)_2Cl_2$$

giving diphenylmethane and dichlorodiphenylmethane, the latter interacting with benzene to form triphenylchloromethane.

[152] H. Schwarz, *Ber.*, 14, 1516-1532 (1881). *J. Chem. Soc. Abs.*, 912 (1881)
[153] Emil and Otto Fischer, *Ber.*, 14, 1942-1944 (1881). *J. Chem. Soc. Abs.*, 62 (1882)
[154] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2)*, 37, 6-11 (1882); *J. Chem. Soc. Abs.*, 621 (1882)
[155] J. Boeseken, *Rec. trav. chim.*, 22, 301-314 (1903). *J. Chem. Soc. Abs.*, 84 (I), 617 (1903)

By the action of chloroform on toluene in the presence of aluminum chloride, Elbs and Wittich [156] obtained, among other products, a substance which they regarded as a dimethylanthracene, m.p. 215-216°. Later, Lavaux [157] showed that this was a mixture of three isomeric dimethylanthracenes and a β-monomethylanthracene. These are caused by the reaction of the ditolylchloromethane first formed with another molecule of chloroform, and subsequent formation of the dimethylanthracene.

Halogen-substituted benzenes react with chloroform to give halogen derivatives of triphenylmethane when subjected to the Friedel-Crafts reaction at room temperature in the absence of solvents. Chloroform, *p*-dichlorobenzene, and *p*-dibromobenzene give normal condensation products.[158]

An attempt has been made [159] to prepare triaryl derivatives of iodine by using iodine trichloride instead of chloroform. The former was caused to undergo a Friedel-Crafts reaction with benzene, but only chloro-substitution products of benzene, together with a small quantity of iodobenzene, were obtained. Derivatives of tervalent iodine were not obtained.

Schwarz [160] tried to react naphthalene with chloroform in the presence of aluminum chloride, and reported that an intense greenish-blue coloration was produced. Later Hönig and Berger [161] studied the same reaction and obtained a pitch-like mass. This was dissolved in benzene; and upon subsequent distillation and recrystallization, they obtained plates, m.p. 189-190° (uncorr.) whose formula appeared to be a multiple of $C_{14}H_{10}$. Two other substances, melting at 170-175° and at 215° were also obtained. Homer [162] reports that the action of chloroform on naphthalene with aluminum chloride does not yield synanthrene, as stated by Hönig and Berger, but β,β-binaphthyl and monoalkyl naphthalenes, because of a secondary reaction between aluminum chloride and trinaphthylmethane.

Bibenzyl is the main product of aluminum chloride-catalyzed condensation of benzene with methylchloroform. No 1,1,1-triphenylethane could be detected among the reaction products.[163]

By the reaction of benzene on ethylene tribromide, $CHBr_2.CH_2Br$, in the presence of aluminum chloride, bibenzyl in moderate quantity is obtained.[164]

Fifty g of ethylene tribromide were dissolved in 400 g of benzene and then gradually added to 25-30 g of aluminum chloride. It was necessary to heat the mixture to the boiling point of the benzene before the reaction began. One of the reaction products was bromobenzene. By distillation under reduced pressure, there was obtained bibenzyl, b_{17} 165-175°, b.p.

[156] K. Elbs and O. Wittich, *Ber.*, **18**, 347-349 (1885); *J. Chem. Soc. Abs.*, 517 (1885).
[157] J. Lavaux *Compt. rend.*, **146**, 345-347 (1908); *J. Chem. Soc. Abs.*, **94** (I), 256 (1908); *Compt. rend.*, **139**, 976-978 (1904) *J. Chem. Soc. Abs.*, **88** (I), 43 (1905).
[158] S. D. Wilson and Hsiao Yun Hsung, *J. Chinese Chem. Soc.*, **4**, 142-148 (1936), *C. A.*, **30**, 8192.
[159] V. Arreguine and E. D. Garcia, *Anales asoc. quim. argentina*, **9**, 121-128 (1921); *J. Chem. Soc. Abs.*, **120** (I), 534 (1921)
[160] H. Schwarz, *Ber.*, **14**, 1516-1532 (1881) *J. Chem. Soc. Abs.*, 912 (1881)
[161] M. Hönig and F. Berger, *Monatsh.*, **3**, 668-672 (1882); *J. Chem. Soc. Abs.*, 68 (1882).
[162] A. Homer, *J. Chem. Soc.*, **97**, 1141-1154 (1910).
[163] M. Kuntze-Fechner, *Ber.*, **36**, 472-475 (1903).
[164] A. Angeblis and R. Anschütz, *Ber.*, **17**, 167-168 (1884); *J. Chem. Soc. Abs.*, 753 (1884)

284°, m.p. 51.5°. Its isomer, diphenylethane, was also one of the reaction products.[165]

1,2,3-tribromo- or -trichloropropane has been reacted with benzene and aluminum chloride; triphenylpropane, together with some dibenzylmethane, $(C_6H_5CH_2.)CH_2(CH_2.C_6H_5)$, was secured.[166]

The reaction of pyrene with aliphatic compounds having up to 4 carbon atoms and at least 2 halogen atoms in the presence of aluminum chloride has been claimed to yield substances imparting fluorescence to oils.[167]

Tetrahalides

The action of carbon tetrachloride on benzene in the presence of aluminum chloride was reported by Friedel and Crafts[168] to yield tetraphenylmethane. A year later, Emil and Otto Fischer[169] claimed that the tetra- compound could not be obtained, but that triphenylmethane, which they identified by changing it into the carbinol, was formed. Later Friedel and Vincent[170] made a more thorough study of the reaction and reported that dichlorophenylmethane and chlorotriphenylmethane were the substances primarily formed. According to Friedel and Crafts,[171] however, the results of the reaction between carbon tetrachloride and benzene vary with the conditions; if the crude product were distilled at high temperatures, even triphenylmethane, as reported by the Fischers, could be obtained. The production of triphenylmethane was reported by various other authors, including Schwarz,[172] and Meyer.[173]

Gomberg[174] showed that the triphenylmethane obtained by these investigators is due to a secondary decomposition of triphenylchloromethane, which is primarily formed. The latter compound is very easily changed into triphenyl carbinol by treatment with water. A 70-87 per cent yield of the triphenyl carbinol was obtained by heating together carbon tetrachloride, benzene, and aluminum chloride, and at the end of the reaction running the well-cooled mixture onto a large quantity of powdered ice contained in a vessel surrounded by a good freezing mixture. To prevent transformation into the carbinol, the product should not be left in contact with water.

Böeseken[175] attempted to explain the mechanism of the reaction, postulating that when benzene is added gradually to a mixture of aluminum chloride and carbon tetrachloride, a liquid additive product of dichlorodiphenylmethane and aluminum chloride is formed, which on further treatment with benzene yields triphenylchloromethane. If the

[165] R. Anschütz, *Ann.*, 235, 333-336 (1886).
[166] A. Claus and H. Merklin, *Ber.*, 18, 2932-2936 (1885).
[167] British P. 485,874 (1938) to I. G. Farbenindustrie; *C. A.*, 32, 8118.
[168] C. Friedel and J. M. Crafts, *Compt. rend.*, 84, 1450-1454 (1877); *J. Chem. Soc. Abs.*, 864 (1877); *Bull. soc. chim.*, 28 (2), 50 (1877).
[169] Emil and Otto Fischer, *Ann.*, 194, 242-302 (1878).
[170] C. Friedel and C. Vincent, *Bull. soc. chim. (2)*, 36, 1 (1881).
[171] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 1, 449-532 (1884).
[172] H. Schwarz, *Ber.*, 14, 1516-1532 (1881); *J. Chem. Soc. Abs.*, 912 (1881).
[173] V. Meyer, *Ber.*, 28, 2778-2795 (1895).
[174] M. Gomberg, *Ber.*, 33, 3144-3149 (1900); *J. Am. Chem. Soc.*, 22, 752-757 (1900); *J. Chem. Soc. Abs.*, 80 (I), 77 (1901).
[175] J. Boeseken, *Rec. trav. chim.*, 24, 1-5 (1905); *J. Chem. Soc. Abs.*, 88 (I), 423 (1905).

addition compound is washed with water, however, dichlorodiphenylmethane is formed. Böeseken obtained an 80-90 per cent theoretical yield of the latter.

Gomberg and Jickling [176] prepared dichlorodiphenylmethane in 90 per cent yield by adding to 135 g of finely divided aluminum chloride in 300 cc of carbon disulfide, 156 g of benzene and an equal volume of carbon tetrachloride in the course of one hour, keeping the temperature below 30°, decomposing the next day with ice, drying the carbon tetrachloride solution with calcium chloride, distilling *in vacuo* and redistilling *in vacuo* with the calculated amount of phosphorus pentachloride to react with the 5-10 per cent of benzophenone in the original distillate.

In the reaction between carbon tetrachloride and benzene five reactions should be possible:

(1) $CCl_4 + C_6H_6 \longrightarrow Cl_3C.C_6H_5 + HCl$

(2) $CCl_4 + 2C_6H_6 \longrightarrow Cl_2C.(C_6H_5)_2 + 2HCl$

(3) $CCl_4 + 3C_6H_6 \longrightarrow ClC.(C_6H_5)_3 + 3HCl$

(4) $CCl_4 + 4C_6H_6 \longrightarrow C(C_6H_5)_4 + 4HCl$

(5) $C_6H_5CCl_3 + C_6H_6 \longrightarrow Cl_2C(C_6H_5)_2 + HCl$

As we have seen, reaction (4), at first advanced by Friedel and Crafts, was subsequently disproved. With regard to reaction (1), Böeseken [177] says that the reason that no trichlorophenylmethane can be detected in the reaction products may be explained by the simultaneous substitution of the first two atoms of chlorine as in reaction (2), or by the rapidity of reaction (5). Dichlorodiphenylmethane is the product obtained under ordinary conditions of the reaction; substantial amounts of triphenylchloromethane are not obtained unless reaction (5) is prevented, as seen in the sudden cooling effected by Gomberg.[178]

Benzophenone in 80-89 per cent theoretical yield can be prepared by the action of benzene on carbon tetrachloride in the cold and subsequent hydrolysis of the benzophenone dichloride by distillation with steam.[179] The reactions proceed thus:

$$2C_6H_6 + CCl_4 \xrightarrow{AlCl_3} C_6H_5CCl_2C_6H_5 + 2HCl$$
$$C_6H_5CCl_2C_6H_5 + H_2O \longrightarrow C_6H_5COC_6H_5 + 2HCl$$

A 68-84 per cent theoretical yield of triphenylmethane was obtained [180] by reacting 3 moles of benzene with 1 mole of carbon tetrachloride and aluminum chloride. Upon adding ether to the reaction product, the triphenylmethane was obtained, according to the equation:

$$3C_6H_6 + CCl_4 + AlCl_3 \longrightarrow (C_6H_5)_3CCl.AlCl_3 + 3HCl$$
$$(C_6H_5)_3CCl.AlCl_3 + (C_2H_5)_2O \longrightarrow (C_6H_5)_3CH + CH_3CHO + C_2H_5Cl + AlCl_3$$

[176] M. Gomberg and R. L. Jickling, *J. Am. Chem. Soc.*, **37**, 2575-2591 (1915); *C. A.*, **10**, 53.
[177] J. Boeseken, *Rec. trav. chim.*, **27**, 5-9 (1908); *J. Chem. Soc. Abs.*, **94** (I), 189 (1908).
[178] M. Gomberg, *Ber.*, **33**, 3144-3149 (1900); *J. Am. Chem. Soc.*, **22**, 752-757 (1900); *J. Chem. Soc. Abs.*, **80** (I), 77 (1901).
[179] C. S. Marvel and W. N. Sperry, "Organic Syntheses," Vol. VIII, *pp.* 26-29 (1928).
[180] J. F. Norris, "Organic Syntheses," Vol. IV, pp. 81-83, 1925.

To a mixture of 292 g of dry benzene and 116 g of dry carbon tetrachloride was added 100 g of anhydrous aluminum chloride. The reaction vessel is immediately cooled and then allowed to stand for 24 hours. Then is added 110 g of anhydrous ether, and the reaction mixture is again allowed to stand for 24 hours. This is decomposed with ice-HCl. One liter of benzene is then added, and the mixture is heated on a steam-bath and boiled for five to ten minutes. The mixture is allowed to cool to 40-50°, when the benzene layer is separated, and washed with 700 cc of warm water containing 25 cc of concentrated hydrochloric acid. After removal of benzene, the residue is distilled and the fraction boiling 190-215°/10 mm is collected. Recrystallization from alcohol gives the pure triphenylmethane in a total yield of 125-154 g.

Norris [181] considers the reaction between ether and the molecular compound of triphenylmethyl chloride and aluminum chloride to proceed thus:

$$(C_6H_5)_3C.Cl + (C_2H_5)_2O \longrightarrow (C_6H_5)_3C.OC_2H_5 + C_2H_5Cl$$
$$(C_6H_5)_3C.OC_2H_5 \longrightarrow (C_6H_5)_3CH + CH_3CHO$$

Butyl ether and ethyl alcohol have the same effect as ether, but ethyl acetate does not. Heating the alkyl ethers or esters of triphenylcarbinol gives an excellent yield of triphenylmethane. The by-product with the ethyl ether is acetaldehyde, with isopropyl ether, acetone. Aluminum chloride and diphenyldichloromethane in ether give benzophenone.

The reaction of carbon tetrachloride with benzene homologs is analogous to that with benzene. Gomberg and Voedisch [182] obtained tritolylchloromethane by the action of aluminum chloride on a mixture of carbon tetrachloride and toluene, the method used being that which has been described for the preparation of the corresponding phenyl compound.[183] Later the tritolylchloromethane was shown to be the tri-*p*-tolyl derivative, m.p. 173°.[184] According to Böeseken [185] the gradual addition of toluene to a mixture of aluminum chloride and carbon tetrachloride results in the production of dichlorotolylmethanes in which the *para* derivative predominates. Gomberg and Todd [185] have also shown that dichloroditolylmethanes are formed in the reaction. These undergo violent decomposition when distillation is attempted. The reaction with *m*-xylene results in a certain amount of resinification,[186] but the crude product, when warmed with acetic acid, yields an oil which was identified as 2,4,2',4'-tetramethylbenzophenone, $C_6H_3(CH_3)_2.CO.C_6H_3(CH_3)_2$.

The action of aluminum chloride and benzene on *sym*-tetrabromo-

[181] J. F. Norris, *Ind. Eng. Chem.*, **16**, 184 (1924); *J. Chem. Soc. Abs.*, **126** (I), 381 (1924) J. F. Norris and R. C. Young, *J. Am. Chem. Soc.*, **46**, 2580-2583 (1924); *C. A.*, **19**, 271

[182] M. Gomberg and O. W. Voedisch, *J. Am. Chem. Soc.*, **23**, 177-178 (1901); *J. Chem. Soc. Abs.*, **80** (I), 374 (1901).

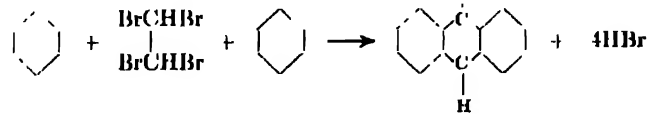
[183] M. Gomberg, *Ber.*, **33**, 3144-3149 (1900); *J. Am. Chem. Soc.*, **22**, 752-757 (1900); *J. Chem. Soc. Abs.*, **80** (I), 77 (1901).

[184] N. E. Tousley and M. Gomberg, *J. Am. Chem. Soc.*, **26**, 1516-1523 (1904); *J. Chem. Soc. Abs.*, **88** (I), 43 (1905).

[185] M. Gomberg and J. D. Todd, *J. Am. Chem. Soc.*, **39**, 2392-2396 (1917).

[186] J. Böeseken, *Rec. trav. chim.*, **24**, 1-5 (1905); *J. Chem. Soc. Abs.*, **88** (I), 423 (1905).

ethane results in the formation of anthracene.[187] Its formation may be explained by the equation:



According to Anschütz,[188] this synthesis of anthracene indicates that the *meso*-carbon atoms in anthracene are probably linked together. The reaction was repeated with toluene, the three xylenes, and with ethylbenzene in place of benzene.[189]

Toluene, *sym*-tetrabromoethane and aluminum chloride yielded a dimethylanthracene, but it was obtained in much smaller quantity than was anthracene from benzene. The xylenes also yielded methylated anthracenes, but in extremely small quantity; no homolog of anthracene could be obtained from ethylbenzene. In all these reactions benzene homologs are also produced. These are due to the action of aluminum chloride on the initial hydrocarbon, and appear to be independent of the *sym*-tetrabromoethane.

It was later shown[190] that the dimethylanthracene formed by the interaction of *sym*-tetrachloroethane, aluminum chloride, and toluene consists of a mixture of dimethylanthracenes, m.p. 240° and 244.5°, respectively, with traces of β-methylanthracene. The yield of dimethylanthracenes is more constant, and is increased from 10-20 to 42 per cent of the theoretical, if the reacting mixture is shaken during the whole course of the reaction.

Lavaux[190] reported that the dimethylanthracenes were the 1,6- and 2,7- isomers. He explained the formation of these two compounds by assuming first the formation of *sym*-ditolyldibromoethane, the loss of two moles of hydrogen bromide, and the consequent ring closure to the 1,6-, 2,7-, or 1,8-dimethylanthracene derivative. The 1,8- isomer was formed in only very small quantities.

From the products of the action of tetrabromo- or chloro-ethane on naphthalene in the presence of aluminum chloride, Homer[191] isolated a hydrocarbon, $C_{22}H_{14}$, m.p. 267.5°, which was thought to be 1,2,7,8-dibenzoanthracene.

Pentachloroethane with benzene and aluminum chloride results in the evolution of hydrogen chloride, and the formation of triphenylmethane and anthracene. When hexachloroethane is used, small quantities of

[187] R. Anschütz and F. Ettabacher, *Ber.*, 16, 1435-1446 (1883); *J. Chem. Soc. Abs.*, 1132 (1883; *Ber.*, 16, 623-624 (1883); *J. Chem. Soc. Abs.*, 809 (1883).
[188] R. Anschütz, *Ann.*, 235, 150-229, 299-341 (1886); *J. Chem. Soc. Abs.*, 52, 150 (1887).
[189] R. Anschütz and H. Immendorff, *Ber.*, 17, 2816-2817 (1884); *J. Chem. Soc. Abs.*, 48, 269 (1885).
[190] J. Lavaux, *Compt. rend.*, 146, 345-347 (1908); *J. Chem. Soc. Abs.*, 94 (I), 256 (1908); *Compt. rend.*, 139, 976-978 (1904); *J. Chem. Soc. Abs.*, 88 (I), 43 (1905); *Compt. rend.*, 146, 135-137 (1908).
[191] A. Homer, *J. Chem. Soc.*, 97, 1141-1154 (1910).

chlorobenzene and anthracene are obtained, besides unaltered benzene and hexachloroethane.[192]

Unsaturated Unsubstituted Alkyl Halides and Aromatic Hydrocarbons

Monohalogenated

The reaction of monohalogenated unsaturated aliphatic hydrocarbons with benzene leads to the formation of saturated hydrocarbons.

Vinyl chloride, a catalyst made from aluminum and mercuric chloride, and benzene have been found to yield chiefly asymmetrical diphenylethane and a small quantity of 9,10-dimethyldihydroanthracene.[193] When vinyl chloride gas is passed into a suspension of 50 g of aluminum chloride in 300 cc of benzene at 0-5° until 90 g of the gas has been added, the main products are asymmetrical diphenylethane and an anthracene-type resin; small amounts of 9,10-dimethyl-9,10-dihydroanthracene are also formed. Very small amounts of aluminum chloride give small yields of the products; however, relatively large amounts cause a diminution in the amount of the diphenylethane compound formed. When the reaction is carried out at 60-70° an increased amount of the anthracene derivative is produced. In the presence of a small amount of mercury, increased production of ethylbenzene occurs, probably because of a reduction of 1-chloro-1-phenylethane, which is considered to be an intermediate product. Styrene or meta-styrene is not produced during the reaction.[194] Styrene polymerizes in the presence of benzene and aluminum chloride, and could not have been an intermediate in the reaction between vinyl chloride and benzene with aluminum chloride.

The reaction of vinyl bromide with benzene has been shown to proceed as follows: To benzene (400-500 g) is added 30 g of aluminum chloride; to this is then introduced, with gentle heating, 50 g of vinyl bromide. A small amount of styrene, b.p. 143-146°, 13 g of ethylbenzene, b.p. 134°, 46 g of *asym*-diphenylethane, and some dimethylanthracene hydride were obtained.[195] The formation of ethylbenzene instead of styrene is an instance of the nearly general rule that in this reaction, instead of the unsaturated, the corresponding saturated aromatic hydrocarbon is formed. With regard to the formation of the other two hydrocarbons, it appears to be most probable that during the reaction an addition of hydrogen bromide to vinyl bromide takes place, with consequent formation of ethylidene bromide, which then reacts to give the diphenylethane and the anthracene derivative.[196]

The reaction of vinyl bromide with benzene was reported[197] to proceed differently if 20 g of aluminum chloride is added in small portions,

[192] A Mouneyrat *Bull soc chim (3)*, 19, 554-556, 557-559 (1898); *J. Chem. Soc. Abs*, 76 (I) 490 (1899)
[193] J Boeseken and M C Bastet, *Rec trav chim*, 32, 184 (1913).
[194] J M. Davidson and A. Lowy, *J. Am. Chem. Soc.*, 51, 2078-2082 (1929), *C.* I, 23, 5471.
[195] R Anschütz, *Ann*, 235, 331-332 (1886)
[196] A. Angeblis and R. Anschütz, *Ber.*, 17, 167-168 (1884); *J Chem Soc. Abs*, 753 (1884).
[197] M. Hanriot and J. Guilbert, *Compt. rend*, 98, 525 (1884), *Ber.*, 17, 208 (1884), *J. Chem Soc Abs.* 733 (1884).

avoiding strong heating, to a mixture consisting of 500 g of vinyl bromide and 230 g of benzene. No hydrogen bromide is given off, and two liquid products are obtained, bromoethylbenzene, $C_6H_5.C_2H_4Br$ (b.p. 145-150°/30 mm), and bis-(bromoethyl) benzene, $C_6H_4(C_2H_4Br)_2$, (b.p. 200-230°/30 mm). Other still higher-boiling brominated products were also formed.

The action of allyl chloride on benzene in the presence of aluminum chloride results in the formation of 1,2-diphenylpropane, b.p. 277-279°.[198] An intermediate formation of (β-chloropropyl) benzene ($C_6H_5CH_2.CHCl.CH_3$) and subsequent reaction with the excess of benzene to form the diphenylpropane is assumed. By varying conditions, a fraction (b.p. 130-200°) may be obtained which consists principally of *n*-propylbenzene.[199]

According to Nenitzescu and Isacescu,[200] the formation of *n*-propylbenzene is due to the use of aluminum chloride which has been "poisoned" by addition of water. Here the catalyst is so weakened that it effects dehydrogenation of a simultaneously formed dihydroanthracene, and a subsequent reduction of the primarily formed (β-chloropropyl) benzene is thereby obtained:

$$C_6H_5.CH_2CHCl.CH_3 \xrightarrow{2H} C_6H_5.CH_2CH_2CH_3 + HCl$$

Polyhalogenated

Condensations of unsaturated polychlorinated aliphatic hydrocarbons with aromatic hydrocarbons have not been thoroughly studied.

In studying the constitution of dibromoethylene, Demole[201] found that a solution of his dibromoethylene reacted with benzene and aluminum chloride to give asymmetrical diphenylethylene, $CH_2{:}C(C_6H_5)_2$, (b.p. 174-176°). He, therefore, ascribed the asymmetrical structure, $CH_2{:}CBr_2$, to his dibromoethylene. The formation of asymmetrical diphenylethylene from vinylidene bromide and benzene was later confirmed by Anschütz.[202]

Reaction of tribromoethylene with benzene and aluminum chloride likewise gives asymmetrical diphenylethylene as the main product. However, some triphenylmethane is also obtained. The production of the former may be explained by cleavage of bromine from tribromoethylene, subsequent addition of hydrogen bromide and reaction of the resulting vinylidene bromide with benzene:

$$\begin{array}{c} CHBr \\ \| \\ CBr_2 \end{array} \longrightarrow \begin{array}{c} CH \\ \| \\ CBr \end{array} \longrightarrow \begin{array}{c} CH_2 \\ \| \\ CBr_2 \end{array} \longrightarrow \begin{array}{c} CH_2 \\ \| \\ C(C_6H_5)_2 \end{array}$$

The formation of triphenylmethane could not be explained.[203]

[198] R. D. Silva, *Compt. rend.*, **89**, 606-608 (1879); *J. Chem. Soc. Abs.*, 259 (1880); *Jahresber. über die Fortschritte der Chemie*, 379-380 (1879). M. Konowalow and S. Dobrowolski, *J. Russ. Phys. Chem. Soc.*, **37**, 548 (1905); *Chem. Zentr.*, 1905, II, 825.
[199] F. Wispek and R. Zuber, *Ann.*, **218**, 374-382 (1883); *J. Chem. Soc. Abs.*, 977 (1883).
[200] C. D. Nenitzescu and D. A. Isacescu, *Ber.*, **66**, 1100-1103 (1933).
[201] E. Demole, *Ber.*, **12**, 2245-2247 (1879); *J. Chem. Soc. Abs.*, 158 (1880).
[202] R. Anschütz, *Ann.*, **235**, 158-160 (1886).
[203] R. Anschütz, *Ann.*, **235**, 336-338 (1886).

Recently, the reaction of vinylidene chloride with aromatic hydrocarbons or with their halogenated derivatives and aluminum chloride has been claimed to result in formation of resinous products.[204] Although some of these appear to be diaryl ethylene compounds, others, from their molecular weight, are assumed to be polymers of such compounds. The reaction of trichloroethylene with an aromatic hydrocarbon containing nuclearly substituted halogen and aluminum chloride leads to the formation of condensation products which may be used in the preparation of non-inflammable compositions from chlorinated rubber.[205]

When aluminum chloride is gradually added to a solution of tetrachloroethylene, $CCl_2{:}CCl_2$, in benzene, and heated at 70°, anthracene is the sole product of the reaction.[206]

Reaction of Aryl Alkyl Chlorides with Aromatic Hydrocarbons

The reaction of aryl alkyl chlorides with an aromatic compound, generally proceeds according to the following equation:

$$RR'Cl + HR'' \longrightarrow RR'R'' + HCl$$

In the reaction of benzyl chloride with benzene, diphenylmethane as the chief product, together with a small quantity of anthracene, is obtained.[207]

$$C_6H_5CH_2Cl + C_6H_6 \longrightarrow C_6H_5CH_2C_6H_5 + HCl$$

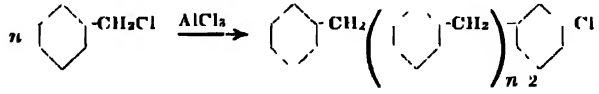
The action of aluminum chloride on benzyl chloride results in a resinous, polymeric form of benzyl chloride.[208] This self-condensation indicates the greater reactivity of benzyl chloride over alkyl halides. In studying the mechanism of the reaction between toluene and benzyl chloride, Steele [209] assumed the formation of a benzyl chloride-aluminum chloride complex. Tronov and co-workers [210] likewise assume that the formation of the complex is the first stage of the reaction between benzyl chloride and benzene. Complex formation between the catalyst and the benzene ring of benzyl chloride, with a consequent increase in the reactivity of the halogen, may explain the much greater reactivity of benzyl chloride as compared with ethyl bromide; the activities of the halogen in the two compounds are approximately equal, but ethyl bromide is incapable of complex formation.

However, Lavaux and Lombard [207] have advanced the following mechanism for the reaction:

$$RCH_2Cl + AlCl_3 \longrightarrow R\,AlCl_2 + CH_2Cl_2$$

[204] U. S. P. 2,135,122 (1938) to G. H. Coleman, C. V. Moore, and G. B. Stratton, to Dow Chemical Co.)
[205] U. S. P. 2,136,270 (1938) to N. Bennett (to Imperial Chemical Industries).
[206] A. Mouneyrat, *Bull. soc. chim. (3)*, 19, 557-559 (1898); *J. Chem. Soc. Abs.*, 76 (I), 490 (1899)
[207] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 1, 480 (1884). C. Friedel and M. Balsohn *Bull. soc. chim. (2)*, 33, 337 (1880). J. Schramm, *Ber.*, 26, 1706-1709 (1893). J. Lavaux and M. Lombard, *Bull. soc. chim. (4)*, 7, 539-542 (1910); *C. A.*, 4, 2448.
[208] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2)*, 43, 53 (1885). C. Radziewanowski, *Ber.*, 27, 3235-3238 (1894). J. Lavaux and M. Lombard, *loc. cit.*
[209] B. D. Steele, *J. Chem. Soc.*, 83, 1470-1490 (1903).
[210] B. V. Tronov, L. V. Ladigina, and I. M. Karpenko, *J. Gen. Chem. (U.S.S.R.)*, (I), 910-916 (1931); *Brit. Chem. Abstracts-A*, 373 (1932).

According to these investigators, the formation of diphenylmethane and of anthracene in the reaction is due to condensation of the dichloromethane with the benzene-aluminum chloride complex. On the other hand, such a mechanism does not explain the self-condensation of benzyl chloride in the presence of aluminum chloride



as it occurs in production of benzyl resins. Or, only two molecules of benzyl chloride may react. Thus, Wertyporoch and Farnik [211] have shown that benzyl chloride with aluminum chloride in nitrobenzene yields *o*- and *p*-chloromethyldiphenylmethanes.

Olivier [212] differs from both theories, assuming no complex formation with either hydrocarbon or benzyl chloride. He bases his explanation, however, on the fact that benzene forms no addition product with aluminum chloride, although the question of aluminum chloride-hydrocarbon complexes is still debatable. Olivier states that the formation of addition products with aluminum chloride may be considered as a poisoning of the catalyst rather than an explanation of the acceleration of the reaction. It was experimentally confirmed by him that benzene, which he assumes forms no addition product with aluminum chloride, reacts readily with benzyl chloride in the presence of the complex, nitrobenzene-aluminum chloride, $C_6H_5NO_2.AlCl_3$, giving a 60 per cent yield of diphenylmethane. The nitrobenzene, joined to the aluminum chloride, does not react at all, and the addition product is a less active catalyst for the reaction than is aluminum chloride itself. That there is decreased effect is shown by the fact that the amount of non-volatile by-products formed is less when the action of the aluminum chloride is moderated by nitrobenzene.

Only very small amounts of the catalyst need to be used in the reaction between benzyl chloride and benzene.[213] Two-tenths mole of benzyl chloride diluted with 1 mole of benzene is dropped very slowly into about 4 moles of benzene in which .02 mole of finely powdered aluminum chloride had been suspended, and the temperature is not allowed to exceed 10°. When half of the benzyl chloride has been added, the liquor containing the aluminum chloride is removed and replaced by 4 moles of pure benzene. (This manipulation is necessary to prevent the diphenylmethane which has been formed from being attacked by the catalyst). The remainder of the benzyl chloride is then added as before. The yield of the diphenylmethane is brought up to 96 per cent in this way, with a minimum formation of anthracene; but the procedure takes about three hours.

[211] E. Wertyporoch and A. Farnik, *Ann.*, 491, 265-273 (1931); *C. A.*, 26, 1275.
[212] S. C. J. Olivier, *Rec. trav. chim.*, 45, 817-818 (1926); *C. A.*, 21, 2883.
[213] J. Böeseken, *Rec. trav. chim.*, 24, 6-18 (1905).

It is interesting to note in this connection that the reaction of benzyl chloride with aromatic hydrocarbons takes place at high temperatures without a catalyst, and that the use of aluminum chloride simply permits the use of lower temperatures.[214]

The use of aluminum with either hydrogen chloride or mercuric chloride for the synthesis of diphenylmethane from benzyl chloride and benzene also has been shown to result in 60-70 per cent yields.[215] A small quantity of aluminum shavings is placed in an excess of benzene; gaseous hydrogen chloride is passed in for twenty minutes, and the mixture allowed to remain until the metal turns brown and a copious evolution of hydrogen begins. The organic halide is then added drop by drop, under cooling. Or, instead of passing hydrogen chloride into the mixture of aluminum shavings and benzene, mercuric chloride may be added. Either of these methods imparts only moderate activity to the catalyst and insures better yields of diphenylmethane by reducing possible side reactions.

The activity of mercuric chloride and aluminum is here explained by complex-formation with the aromatic hydrocarbon, *e.g.*,

$$C_6H_6 + Al + 2HgCl_2 \longrightarrow C_6H_5.AlCl_2HgCl + Hg$$

This complex is assumed to act as a catalyst.[216]

Friedel[217] reported that if aluminum chloride is added slowly to a mixture of toluene and benzyl chloride, benzyltoluene is formed:

$$C_6H_5CH_2Cl + C_6H_5CH_3 \longrightarrow C_6H_5CH_2.C_6H_4CH_3 + HCl$$

However, if the benzyl chloride is added to a mixture of toluene and aluminum chloride, a solid hydrocarbon resembling anthracene was obtained. This may be caused by a sudden reaction involving cleavage of the alkyl groups and addition of the rings present. Later it was found that the solid hydrocarbon produced was a mixture of 1,6- and 2,7-dimethylanthracene, and the formation of benzyltoluene was confirmed.[218]

Using a substituted benzyl chloride and toluene, the following was found to occur:

$$CH_3C_6H_4CH_2Cl + C_6H_5CH_3 \longrightarrow CH_3C_6H_4CH_2.C_6H_4CH_3 + HCl$$

With ditolylmethane, small amounts of the same dimethylanthracene were found to be present. These may be due to a partial splitting up of the aromatic chloride with the formation of a complex, $R.AlCl_2$, and liberation of CH_2Cl_2, which then reacts with any free hydrocarbon present, or in its absence with the foregoing complex.

The reaction proceeds by replacement of the chlorine atom of the

[214] C. D. Nenitzescu, D. A. Isacescu, and C. N. Ionescu, *Ann.*, **491**, 210-220 (1931); *C. A.*, **26**, 1257.
[215] C. Radziewanowski, *Ber.*, **28**, 1135-1140 (1895).
[216] J. N. Ray, *J. Chem. Soc.*, **117**, 1333-1339 (1920); *C. A.*, **15**, 1133.
[217] C. Friedel and J. M. Crafts, *Compt. rend.*, **84**, 1450-1454 (1877); *J. Chem. Soc. Abs.*, **864** (1877); C. Friedel, *Bull. soc. chim.*, **37** (2), 530 (1882).
[218] J. Lavaux and M. Lombard, *Bull. soc. chim.*, **7**, 539-542 (1910); *C. A.*, **4**, 2448.

benzyl chloride with a substituted or unsubstituted mono- or polynuclear aromatic compound.[216] With biphenyl, 4-benzylbiphenyl was formed:

$$C_6H_5CH_2Cl + C_6H_5C_6H_5 \longrightarrow C_6H_5CH_2C_6H_4C_6H_5 + HCl$$

Similarly, 1-benzylnaphthalene is produced from naphthalene and 2,4,6-trimethyldiphenylmethane from mesitylene. It is interesting to note that the reaction proceeds in the same way with an ether, anisole and benzyl chloride yielding *p*-methoxydiphenylmethane.

The condensation of benzyl chloride with naphthalene in the presence of aluminum chloride has been extensively studied by Dziewonski and co-workers,[219] who have found that mono- and di-substitution results.

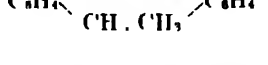
Products of the reaction of aralkyl or cycloalkyl halides with naphthalene and aluminum chloride may be used as plasticizers for vinyl resins.[220]

The length of the side-chain of the aralkyl chloride does not influence the course of the reaction, unless the side-chain is long enough to permit ring-closure. 1-Chloro-2-phenylethane, benzene, and aluminum chloride give bibenzyl.[221]

$$C_6H_5CH_2CH_2Cl + C_6H_6 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + HCl$$

An 85 per cent yield of bibenzyl has been obtained. A study of the reaction has revealed no intermediate formation of styrene.[216]

1-Chloro-1-phenylethane undergoes a similar reaction with benzene, the product being asymmetrical diphenylethane, together with ethylbenzene, and 9,10-dihydro-9,10-dimethylanthracene:



Intermediate formation of styrene was assumed in these reactions.[222] 1-Chloro-3-phenylpropane undergoes normal reaction with *o*-xylene and aluminum chloride, giving a 60 per cent yield of phenylxylylpropane, $C_6H_5.(CH_2)_3.C_6H_3(CH_3)_2$. However, with 1-phenyl-4-chlorobutane or with 1-phenyl-5-chloropentane, Friedel-Crafts condensation does not occur. Instead, the catalyst effects ring closure of the aralkyl halides, yielding tetralin and phenylcyclopentane, respectively.[223]

Only small yields of benzyltoluene have been obtained in the reaction of *m*-methylbenzyl chloride with benzene and aluminum chloride[224]:

$$CH_3C_6H_4CH_2Cl + C_6H_6 \longrightarrow CH_3C_6H_4CH_2C_6H_5$$

[219] K. Dziewonski and J. Mosrew, *Bull. intern. acad. polon. sci.*, 283-291 (1928); *C. A.*, **23**, 3220. K. Dziewonski, J. Mosrew, S. Lepiankewicz, and L. Suchen, *Bull. intern. acad. polon. sci. A.*, 650-657 (1929); *C. A.*, **25**, 1515. K. Dziewonski and S. Wodelski, *Roczniki Chem.*, **12**, 366-377 (1932); *Brit. Chem. Abstracts-A*, 830 (1932).

[220] British P. 450,592 (1936) to I. G. Farbenindustrie; *C. A.*, **32**, 6359.

[221] R. Anschütz, *Ann.*, **235**, 329-332 (1886).

[222] J. Schramm, *Ber.*, **26**, 1706-1709 (1893); *J. Chem. Soc. Abs.*, **64** (I) 561 (1893).

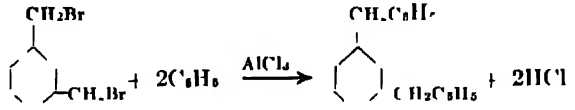
[223] J. von Braun and H. Deutsch, *Ber.*, **45**, 2171-2188 (1912); *cf.* J. von Braun and H. Deutsch, *Ber.*, **45**, 1267-1274 (1912); *C. A.*, **6**, 2603.

[224] P. Senff, *Ann.*, **220**, 225-253 (1883).

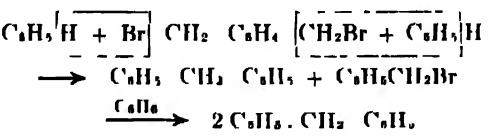
In a comparison of the reaction of benzyl chloride and of *m*-chlorobenzyl chloride on benzene in the presence of aluminum chloride in nitrobenzene, it has been found that benzyl chloride reacts more rapidly than the chlorine-substituted compound [225] From this it may be assumed that the more negative the chlorine atom of the side chain, the more rapidly the reaction proceeds.

Chlorine-substituted benzyl chlorides have been condensed with various aromatic compounds to give products which have been found useful in industry. 3,4-Dichlorobenzyl chloride with naphthalene gives 3,4-dichlorobenzylnaphthalene, which may be used as plasticizer for vinyl resins.[226] Chlorinated benzyl chlorides have been condensed with chlorobenzene to yield oils having high dielectric constants [227]

The condensation of *m*-bis (bromoethyl) benzene with benzene and aluminum chloride does not take the expected course·



Instead, the main reaction product is diphenylmethane; and small amounts of *p*-dibenzylbenzene, anthracene, and mixtures of very viscous, fluorescent liquids are also produced [228] The production of diphenylmethane has been assumed to result from the following series of reactions.



The production of *p*-dibenzylbenzene and of anthracene may be explained by the fact that these compounds have been shown to be formed by the action of aluminum chloride on diphenylmethane.[229]

Dihalogeno- Aralkyls

The reaction of dihalogeno- aralkyls with aromatic compounds in the presence of aluminum chloride results in the substitution of both chlorine atoms:

$$RCHCl_2 + 2R' \longrightarrow RCHR'_2$$

Linebarger [230] reports that the action of benzene on benzal chloride results in the formation of triphenylmethane and diphenylanthracene dihydride as the principal reaction products. Twenty-five g of aluminum

[225] S. C J. Olivier and G Berger, *Rec trav chim*, 45, 710-721 (1926); *C A*, 21, 2887.
[226] British P 480 592 (1938), to I G Farbenindustrie; *C A.*, 32, 6350
[227] British P 434 072 (1935) to British Thomson-Houston Co, Ltd, *C. A*, 30, 489 French P 770,848, *C A*, 29, 814 and U S P 2,012,302 to General Electric Co., *C. A.*, 29, 6607.
[228] F Reindel and F Siegel, *Ber*, 56, 1550-1557 (1923); *J. Chem. Soc. Abs.*, 124 (I), 916 (1923).
[229] R Scholl and C Seer, *Ber* 55, 330-341 (1922)
[230] C. E Linebarger, *Am Chem. J.*, 13, 556-559 (1891); *J Chem, Soc. Abs*, 62 (I), 719 (1892).

chloride was added to a mixture of 200 g of benzal chloride and 1000 g of benzene, and the whole was heated at about 50° for two hours, at which time a little less than the theoretical amount of hydrogen chloride had been given off. The reaction was completed by boiling for a few minutes, and the product was washed with water and fractionated. The fraction passing over at 300-360° is chiefly triphenylmethane. The yield of the latter is about 30 per cent of the benzal chloride used. Only traces of diphenylmethane are formed if the materials are pure. Böeseken [231] used 30 g of benzal chloride with benzene and obtained 11 g of triphenylchloromethane, 6 g of triphenylmethane, and 3 g of diphenylmethane. The formation of triphenylchloromethane may be attributed to the intermediate formation of diphenylchloromethane, which decomposes to give diphenylmethane and dichlorodiphenylmethane:

$$2(C_6H_5)_2CHCl \longrightarrow (C_6H_5)_2CH_2 + (C_6H_5)_2CCl_2$$

The dichlorodiphenylmethane thus formed reacts with another molecule of benzene to form triphenylchloromethane. Böeseken showed that 25 g of dichlorodiphenylmethane combined with benzene to give 10.7 g of triphenylchloromethane and 7.8 g of diphenylmethane.

Condensation of benzal chloride with *o*-xylene and aluminum chloride has been shown to proceed with formation of 9,10-diphenyl-2,3,6,7-tetramethylanthracene, together with much tar.[232] The reaction was performed under cooling, using tetrachloroethane as solvent.

Styrene dibromide, $C_6H_5CHBr.CH_2Br$, has been reacted with benzene, using carbon disulfide as solvent and aluminum chloride as catalyst. Bibenzyl, m.p. 51°, was obtained; the expected triphenylethane was not formed, for the styrene dibromide had probably lost hydrogen bromide, forming β-bromostyrene, $C_6H_5CH{:}CHBr$; and the latter had reacted to give the reduction product, bibenzyl, instead of the expected stilbene.[233]

However, from β-bromostyrene dibromide, $C_6H_5CHBr.CHBr_2$, under like conditions, tetraphenylethane was obtained, with normal substitution of all halogen. Stilbene dibromide, $C_6H_5.CHBr.CHBr.C_6H_5$, has been found to give a quantitative yield of tetraphenylethane. Tolane dibromide, $C_6H_5.CBr{:}CBr.C_6H_5$, likewise readily reacts with benzene and aluminum chloride to give tetraphenylethane.[234]

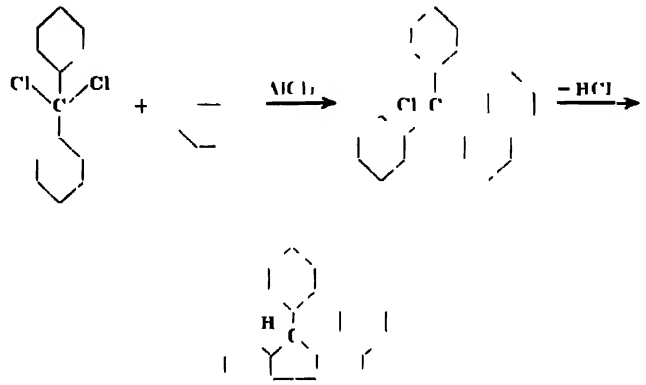
Benzotrichloride and benzene with metal chlorides has been reported to yield not the expected tetraphenylmethane according to the equation,

$$C_6H_5CCl_3 + 3C_6H_6 \longrightarrow C(C_6H_5)_4 + 3HCl$$

but only triphenylmethane.[235] The reaction is here comparable to that of carbon tetrachloride with benzene, in which triphenylmethane is formed.

[231] J. Boeseken, *Rec. trav. chim.*, 22, 301-314 (1903). *J. Chem. Soc. Abs.*, 84 (1), 617; *Rec. trav. chim.*, 23, 101 (1904).
[232] E. Barnett, *J. Chem. Soc.*, 848 (1939)
[233] R. Anschütz, *Ann.*, 235, 338-339 (1886); *cf.* J. Schramm, *Ber.*, 26, 1706-1709 (1893); *J. Chem. Soc. Abs.*, 64 (I), 861 (1893).
[234] R. Anschütz, *Ann.*, 235, 304-311 (1886).
[235] O. Doebner and G. Magatti, *Ber.*, 12, 1462-1468 (1879).

Condensation of diphenyldichloromethane with naphthalene and aluminum chloride may proceed with replacement of one chlorine atom to give diphenyl-α-naphthylchloromethane.[236] Or the reaction may proceed further with elimination of hydrogen chloride, and the formation of a fluorene derivative:



In this way is obtained 9-phenyl-1,2-benzofluorene, together with the isomeric 9-phenyl-3-4-benzofluorene.[237]

Reaction of Alicyclic Chlorides with Aromatic Hydrocarbons

Alicyclic chlorides may be used in the synthesis of hydrocarbon homologs. The Friedel and Crafts reaction is just as applicable to the chlorine compounds of the cyclohexanes as it is to those of the aliphatic derivatives.[238] The phenylcyclohexanes so produced have all the properties of aromatic compounds with an aliphatic side chain. A 50 per cent yield of phenylcyclohexane is secured by reacting cyclohexyl chloride, benzene, and aluminum chloride.[239] The pure hydrocarbon (b.p. 115°/15 mm) in 76 per cent yield may be obtained by completing the reaction under short heating at 100°.[240] When toluene is treated with chlorocyclohexane in the presence of aluminum chloride, there results a mixture of isomeric tolylcyclohexanes which cannot be separated by fractional distillation.[239] One of these has been isolated as the sodium sulfonate. A substituted cyclo-compound may be used. For example, chloromethylcyclohexane reacts with benzene in the presence of aluminum chloride to yield 3-phenyl-1-methylcyclohexane, $H\,C\begin{matrix} CH_2 . CH . C_6H_5 \\ \diagdown \\ \diagdown \\ CH_2CH_2 . CH_2 \end{matrix}CH_2$, a liquid with an odor resembling that of lemon (b.p. 249°/730 mm).

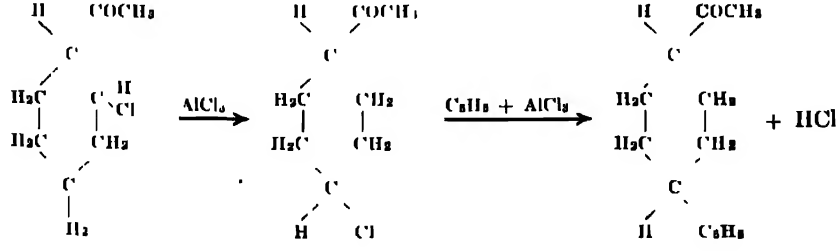
[236] M. Gomberg, *Ber.*, 37, 1637 (1904)
[237] E. Clar, *Ber.*, 63, 512-517 (1930); *C. A.*, 24, 3007
[238] N. Kursanoff, *J. Russ. Phys.-Chem. Soc.*, 38, 1304-1316 (1906), *J. Chem. Soc. Abs.*, 92 (1) 600 (1907)
[239] N. Kursanoff, *Ann.*, 318, 309-326 (1901)
[240] H. A. Mayes and E. E. Turner, *J. Chem. Soc.*, 500-508 (1929)

m-Xylene and cyclohexyl bromide condense in the presence of aluminum chloride to yield a dicyclohexyl-*m*-xylene, $C_{20}H_{30}$ (m.p. 104°), and 5-cyclohexyl-*m*-xylene (b.p. 265-266°/748 mm).[241]

The alicyclic halides may be caused to react with a chlorinated aromatic hydrocarbon, the substitution occurring in the *p*-position. By slowly adding 62 g of cyclohexyl chloride to a well-shaken mixture of 160 g of chlorobenzene and 14 g of aluminum chloride which has not been cooled, a 74-g yield of *p*-cholorophenylcyclohexane (b.p. 145°/19 mm) can be obtained.[242] The bromo-compound (b.p. 160°/23 mm) may be similarly prepared.

Cyclopentyl chloride acts as does the cyclohexyl compound. A 43 per cent yield of phenylcyclopentane (b.p. 217°) from cyclopentyl chloride and benzene, has been reported.[243] Bornyl chloride has been reacted with benzene and with toluene. Five g of aluminum chloride was added to 172 g (1 mole) of bornyl chloride in 1170 g of benzene. The reaction was carried out at room temperature and at 250-300 mm. The fraction b. 117-118° was shown to be bornyl-benzene.[244] In the action of bornyl chloride with toluene, a mixture of *m*- and *p*-bornyltoluene is obtained in good yield.[245]

In the reaction of 2-chloro-1-acetylcyclohexane with benzene and aluminum chloride, migration of halogen occurred preliminary to the condensation, for the product was 4-phenyl-1-acetylcyclohexane, instead of the expected 2-phenyl isomer.[246] The reaction probably occurred according to the scheme:



Halogen migration was also found to occur in the condensation of 1,2-dibromo- or -dichloro-cyclohexane with benzene. Here halogen migrated to either the *p*- or *m*-position, so that the product consisted of both *p*- and *m*-diphenylcyclohexane.[247]

[241] M. Battegay and M. Kappeler, *Bull. soc. chim. (4)*, 35, 989-996 (1924); *J. Chem. Soc. Abs.*, (I), 1177 (1924).

[242] H. A. Mayes and E. E. Turner, *loc. cit.* J. H. Brown and C. S. Marvel, *J. Am. Chem. Soc.*, 59, 1175-1176 (1937). C. S. Marvel and C. S. Hinnel *Ibid.*, 62, 1550-1554 (1940).

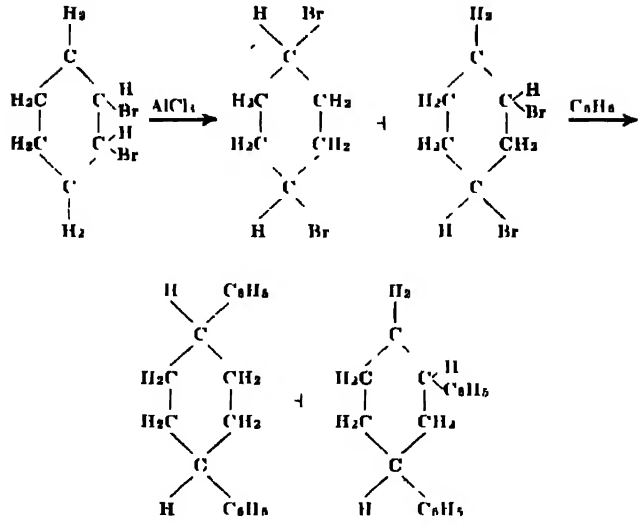
[243] N. D. Zelinsky and I. N. Titz, *Ber.*, 64, 183-188 (1931); *Brit. Chem. Abstracts*-A, 339 (1931) For cyclopentyl derivatives of naphthalene and tetralin, see E. S. Pokrovskaya and R. Ya. Sushchik, *J. Gen. Chem. (U.S.S.R.)*, 9, 2291-2301 (1939); *C. A.*, 34, 5433.

[244] L. Kamieński and P. Wierzchowski, *Roczniki Chem.*, 15, 92-98 (1935).

[245] L. Kamieński and P. Lewiowna, *Roczniki Chem.*, 14, 1348-1353 (1934); *C. A.*, 29, 6226.

[246] C. D. Nenitzescu and I. G. Gavat, *Ann.*, 519, 260-271 (1935).

[247] C. D. Nenitzescu and D. Curcaneanu, *Ber.*, 70, 346-348 (1937).



The aluminum chloride induced migration of halogen resembles that noticed in Friedel-Crafts alkylations of halogenated benzenes.[248]

Replacement of Nuclear Halogen

Although replacement of nuclear halogen in Friedel-Crafts hydrocarbon synthesis is not common, several instances dealing with reactions of this type have been reported. Since such condensations involve loss of halogen from the ring they occur only when the halogen is sufficiently labile to permit replacement. Halogen migration induced by aluminum chloride is discussed in a separate section.*

It has been shown that aluminum chloride may catalyze the migration of a bromine atom from the nucleus of one aromatic compound to another. Thus tribromophenol heated with benzene and aluminum chloride gives bromobenzene and phenol. Under the same conditions trichlorophenol fails to react.[251] Here mobility of the bromine is achieved, but Friedel-Crafts condensation does not occur. Chlorine in the nucleus is not as easily affected by aluminum chloride as is bromine.[252] If the mobility of the halogen in the nucleus is an indication of possible replacement in Friedel-Crafts condensation, nuclear bromine should be more easily replaced than nuclear chlorine. Recent work [253] dealing with the condensation of *p*-fluorophenol with benzene in the presence of aluminum chloride indicates that fluorine in the ring is more labile than either bromine or chlorine.

[248] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, **10**, 411-424 (1887); *J. Chem. Soc. Abs.*, **52**, 1101 (1887)

* See Chapter 15.

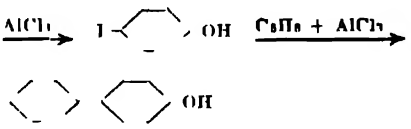
[251] M. Kohn and N. I. Muller, *Monatsh.*, **30**, 407-409 (1909); *C. A.*, **4**, 309.

[252] M. Copisarow and C. N. H. Long, *J. Chem. Soc.*, **119**, 442-447 (1921); *C. A.*, **15**, 2072.

[253] A. W. Weston and C. M. Suter, *J. Am. Chem. Soc.*, **61**, 2556-2557 (1939).

Replacement of halogen in the nucleus is a function of the individual halogen employed, of the aromaticity of the hydrocarbon which it replaces, and finally of the compound with which it reacts. As the aromaticity of the halogenated hydrocarbon is increased, the halogen is rendered increasingly labile. Hence most instances of replacement of nuclear halogen deal with condensations effected with polynuclear compounds.

Condensation of *p*-fluorophenol with benzene occurs in presence of aluminum chloride. During de-ethylation of *p*-fluorophenetole, by heating with aluminum chloride in benzene solution, the production of a considerable amount of a phenolic product, m.p. 153-156°, was noticed.[254] This same product was also obtained in an attempted de-ethylation of 4-fluoro-2-*n*-amylphenetole. Later work showed that this compound was *p*-hydroxybiphenyl. The *p*-fluorophenol, produced upon cleavage of the alkoxy- group, had condensed with the solvent:



This course of the reaction was substantiated by reacting 3 g of *p*-fluorophenol with benzene in the presence of 7 g of aluminum chloride. One g of hydroxybiphenyl was obtained. It was thought that the condensation may have proceeded through intermediate formation of *p*-chlorophenol, but the latter was shown to have no activity toward benzene in the presence of aluminum chloride. A like condensation also did not occur with *p*-fluorophenol and toluene or chlorobenzene.[253]

The condensation of 5-bromo-1,2,4-trimethoxybenzene in the presence of aluminum chloride to form 2,3,5,2′,3′,5′-hexamethoxybiphenyl indicates replacement of nuclear halogen, probably proceded by cleavage and migration of the bromine atom.[255]

Another example of replacement of nuclear halogen from the benzene ring is the condensation of bromobenzene with naphthalene in the presence of aluminum chloride to give a 20 per cent theoretical yield of α-phenylnaphthalene.[256] The reaction was effected by heating for twelve hours at 70-80°. Since reactions of this type are more common with halogen derivatives of polynuclear compounds than with halogeno-benzenes, the condensation may have proceeded with intermediate migration of bromine from the benzene nucleus to that of naphthalene, and subsequent reaction of the halogenated naphthalene with benzene. Another explanation of the reaction may be that the halogenated naphthalene was formed directly from the bromobenzene. The action of aluminum

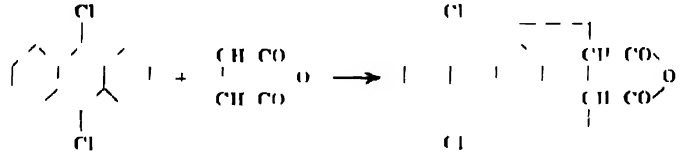
[254] C. M. Suter, E. J. Lawson, and P. G. Smith, *J. Am. Chem. Soc.*, **61**, 161-165 (1939).
[255] W. Baker and C. Evans, *J. Chem. Soc.*, 372-375 (1938).
[256] F. D. Chattaway, *J. Chem. Soc.*, **63**, 1185-1190 (1893).

chloride on bromobenzene has been shown to result in migration, condensation, and pyrogenic-like fission of the benzene nucleus, leading to the formation of bromonaphthalene.[257] The production of α-phenylnaphthalene may thus be due to such intermediate formation of bromonaphthalene, and subsequent condensation with the dehalogenated hydrocarbon.

Reaction of halogenated naphthalene and benzene proceeds smoothly. α-Chloronaphthalene with benzene and aluminum chloride gives a 40 per cent yield of α-phenylnaphthalene, together with a small amount of the β isomer. A similar reaction takes place when α-bromonaphthalene is substituted for the chloro- compound, but the yield is not so good.[258]

In condensation of β-chloro- or β-bromonaphthalene with benzene in the presence of excess of aluminum chloride, the product is α-phenylnaphthalene instead of the β isomer. Here migration of β-halogen to the α position obviously occurs during the reaction.[259]

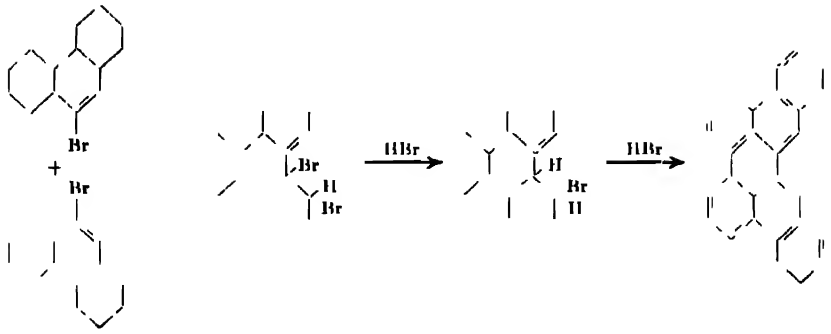
It has been found that by adding maleic anhydride to dichloroanthracene, a compound results in which the chlorine atoms have been rendered so mobile that reaction occurs with aluminum chloride and benzene or *m*-xylene.[260] The addition of maleic anhydride to 9,10-dichloro-anthracene results in the formation of endo-9,10-dichloro-9,10-(α,β-succinic anhydride) anthracene:



Upon suspending this compound in benzene and treating with aluminum chloride, 9,10-diphenylanthracene, m.p. 248°, is easily obtained. Similarly, using *m*-xylene instead of benzene, di-9,10-*m*-xylylanthracene, m.p. 290°, may be prepared. The presence of the anhydride activates the chlorine atoms so that the Friedel-Crafts condensation is possible. Since the anhydride addition products are easily decomposed by heat into their components, this provides a good method for the preparation of anthracene derivatives.

Halogenated polynuclear hydrocarbons may condense with themselves under the influence of aluminum chloride. 9-Bromophenanthrene, in benzene solution, treated with aluminum chloride at room temperature yields 2,3,10,11-dibenzoperylene, the condensation occurring with intermediate migration of bromine[261]:

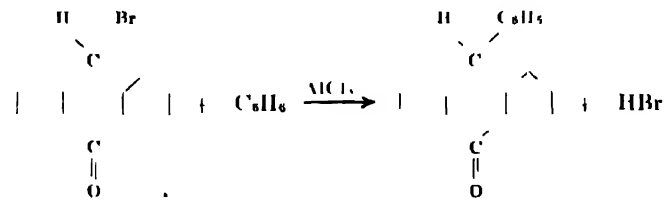
[257] M. Copisarow and C. N. H. Long, *J. Chem. Soc.*, 119, 442-447 (1921).
[258] F. D. Chattaway, *loc. cit.*; *cf.* Armstrong and Wynne, *Proc. Chem. Soc.*, 85 (1890).
[259] F. D. Chattaway and W. H. Lewis, *J. Chem. Soc.*, 65, 869-875 (1894).
[260] E. Clar, *Ber.*, 64, 2194-2200 (1931).
[261] E. Clar, *Ber.*, 65, 846-858 (1932); *C. A.*, 26, 4046 (1932).



The reaction resembles the Scholl condensation; here, however, we have dehydrohalogenation instead of dehydrogenation. Yields of the dibenzoperylene are much lower if the preparation is effected by condensation of phenanthrene in the presence of aluminum chloride, and may be increased only by conducting the reaction in the presence of also an oxidizing agent, such as tin tetrachloride.

Mono, or di-halogenated chrysenes condense upon treatment with aluminum chloride to give dinaphthoperylenes.[262]

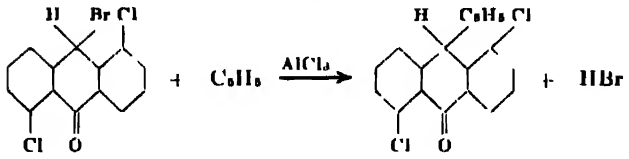
Nuclear halogen may also be replaced in the anthrone series. From 32 g of 9-bromoanthrone, 16 g of 9-phenylanthrone has been obtained according to the equation [263]:



A considerable amount of resinous products is obtained in the reaction. 9-Phenyl-9-chloroanthrone or 9,9-dichloroanthrone yields 9,9-diphenylanthrone by condensation with benzene and aluminum chloride.[264]

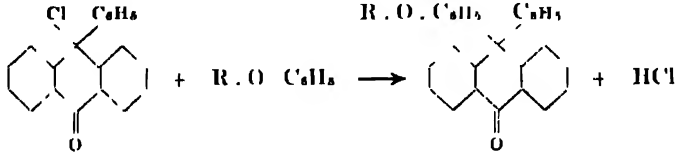
Bromine in the nucleus is more easily replaced than chlorine in aluminum chloride-catalyzed condensations.[257] In the reaction of 2,3- or 1,4-dichloro-10-bromoanthrone with benzene and aluminum chloride, only the bromine is replaced, the products being 2,3- or 1,4-dichloro-10-phenylanthrone.[258a] 1,5-Dichloro-9-bromoanthrone likewise gives almost a quantitative yield of 1,5-dichloro-9-phenylanthrone [259a]:

[262] U. S. P. 2,126,360 (1938) to H. Vollmann and H. Becker (to General Aniline Works).
[263] E. Barnett and J. W. Cook, *J. Chem. Soc.*, 123, 2631-2642 (1923).
[264] A. Haller and A. Guyot, *Compt. rend.*, 121, 102-106 (1895); *J. Chem. Soc. Abs.*, 68 (1), 671 (1895); *Bull. soc. chim. (3)*, 17, 877 (1897).
[258a] E. Barnett, N. F. Goodway, and T. H. W. Savage, *Brit.*, 64, 2185-2194 (1931); *Brit. Chem. Abstracts-A*, 1294 (1931).
[259a] E. Barnett and M. A. Matthews, *Ber.*, 59, 670-679 (1926).



According to Barnett and Matthews,[259a] the presence of chlorine in the nucleus has a stabilizing influence, so that here no resinous products, such as those formed with 9-bromoanthrone, are obtained.

Chlorophenylanthrone has been condensed with anisole and phenetole in the presence of aluminum chloride with replacement of chlorine[260a]:



Dyes are made by heating chloro- derivatives of benzanthrone with aluminum chloride in the presence of an aromatic hydrocarbon or a halogen derivative as solvent. The products are dark-colored pastes or powders that are soluble in hydrocarbons, fats, oils, and waxes to give yellow, red, or brown colorations.[261a]

Substituted Alkyl Halides in Friedel-Crafts Condensations

In Friedel-Crafts hydrocarbon synthesis, the hydrocarbon containing replaceable halogen is generally referred to as the alkylating agent. Condensations in which the alkylating agent contains a halogen substituent have already been cited. In reactions with aralkyl halides the alkylating agent has an aromatic hydrocarbon residue as a substituent. Early investigators readily visualized the application of the Friedel-Crafts reaction to the introduction of aryl groups into various oxygenated compounds by the condensation of a halogen derivative of the compound with an aromatic hydrocarbon. Similar reactions were anticipated with halogen derivatives of compounds of nitrogen, phosphorus, and organometallic compounds. In many cases results were disappointing. Side reactions, due to the action of aluminum chloride on the halogenated compound itself, preceded replacement of halogen. Since nuclear halogen is difficultly displaced, the condensation usually could not be extended to compounds in which the only halogen present was in the ring.

A summary is here given of attempts to use the Friedel-Crafts synthesis for replacement of halogen in the halogenated derivatives of

[259a] L. Tetry, *Compt. rend.*, **128**, 1406-1407 (1899); *J. Chem. Soc. Abs.*, **76** (I), 818 (1899).
[261a] Brit. P. 501 742 (1939) to I. G. Farbenindustrie; *C. A.*, **33**, 6607.

Esters
Acids and lactones
Ketones
Ethers
Aldehydes
Nitrogeneous compounds
Compounds of sulfur
Compounds of selenium, phosphorus, arsenic, and silicon.

Condensations cited here should normally proceed:

$$RH + R'X \longrightarrow RR' + HX$$

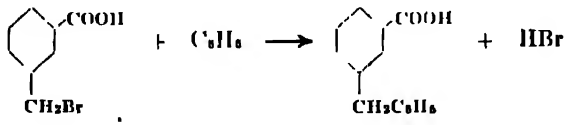
where *R* is an aromatic hydrocarbon or a derivative thereof and R'X is a halogenated derivative of one of the groups of compounds listed above. They are, therefore, closely related to Friedel-Crafts hydrocarbon syntheses. Condensations in which the halogenated component is an acyl halide,

$$R + R'COCl \longrightarrow RCOR' + HCl$$

are not included here. The scope of this reaction has warranted a separate chapter in this book.*

Reaction of Chloro-Esters with Hydrocarbons

Although the ester group may be considered to have an inhibiting action in the Friedel-Crafts synthesis, the presence of very active groups often makes reaction possible. Thus bromo-metatoluic acid and benzene with aluminum chloride gives *m*-benzylbenzoic acid:



Gentle warming until all hydrogen bromide has been evolved gives a 50 per cent yield, calculated on the toluic acid used before bromination.[262a]

Under the influence of aluminum chloride, chloromethylene dibenzoate condenses with benzene, yielding the benzoyl derivative of benzohydrol:

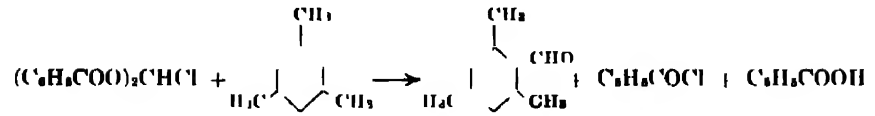
$$(C_6H_5COO)_2CHCl + C_6H_6 \longrightarrow C_6H_5COO.CH(C_6H_5)_2 + CO_2$$

The dibenzoate, $(C_6H_5COO)_2CHC_6H_5$, is probably formed as intermediate product, but all efforts to isolate it proved unsuccessful.[263a] With mesitylene instead of benzene, 2,4,6-trimethylbenzaldehyde was obtained, the reaction probably proceeding thus:

* See Chapter 6.

[262a] P. Senff, *Ann.*, **220**, 225-253 (1883).

[263a] F. Wenzel and L. Bellak, *Monatsh.*, **35**, 965-971 (1914); *J. Chem. Soc. Abs.*, **106** (I), 534 (1915).



Dibenzoates of the type $R\,CH(OOC.C_6H_5)_2$ are probably formed as intermediate products during the reaction, but again all attempts to isolate them proved unsuccessful.

In the preparation of benzene homologs by the Friedel-Crafts reaction, alkyl halides may be replaced by esters of chlorocarbonic acid Thus, ethyl chlorocarbonate, $ClCOO\,C_2H_5$, and benzene with aluminum chloride give ethylbenzene.[264a] A series of alkylations of this nature has been studied.[265] Using a mixture of 20 g of benzene, 5 g of methyl chlorocarbonate, and 13 g of aluminum chloride, 2 g of toluene and 1 g of *m*-xylene were obtained. In the same way *p*-xylene and 1,3,4-trimethylbenzene were prepared from toluene. When the ethyl ester was used with toluene, *p*-diethylmethylbenzene was chiefly formed *m*-Xylene and the ethyl ester gave 1,3-dimethyl-5-ethylbenzene From *p*-xylene, was obtained ethyl-*p*-xylene, an oil boiling 183-185°. Cumene yielded a dimethylcumene, boiling 195-210°. No definite compounds could be obtained from ethyl chlorocarbonate with halogenated aromatic hydrocarbons or naphthalene. Better yields were obtained using the higher homologs of the chlorocarbonic esters with benzene and toluene Thus, from benzene and isobutyl chlorocarbonate a 28 per cent yield of dibutylbenzene, together with a 15 per cent yield of tributylbenzene, was secured. Amyl chlorocarbonate and toluene gave a 30 per cent yield of amyltoluene, boiling 205-210°. The difference in orientation of the entering alkyl group obtained by using alkyl chloride and by using chlorocarbonic ester is apparent:

Predominant Substitution

Methyl ester and benzene	*m*-di-substituents
Ethyl ester and benzene	*p*-di-substituents
Esters and toluene	*p*-di-substituents
Esters and *m*-xylene	*sym*-tri-substituents
Alkyl halide and benzene	*m*- and *p*-di-substituents
Alkyl halide and toluene	*o*- and *m*-compounds
Alkyl halide and *m*-xylene	*asym*-compounds

The condensation of the ethyl ester of trichloroacetic acid with benzene and aluminum chloride has been reported to take an interesting course, with formation of fluorene-9-carboxylic acid.[266] One part of the ester of trichloroacetic acid, 10 parts of benzene, and 3 parts of aluminum chloride are allowed to stand for twelve hours at ordinary temperature, and then heated on the water-bath until evolution of hydrogen chloride

[264a] E H Rennie, *J Chem Soc*, 41, 33 (1882) C Friedel and J M Crafts, *Ann. chim phys* (6) 1, 527 (1884)

[265] F. Kunckell and G Ulex, *J prakt. Chem*, 86, 518-520 (1912); *J. Chem. Soc. Abs.*, 104 (I), 29 (1913); *J prakt Chem.*, 87, 227-236 (1913); *C A.*, 7, 2210 (1913)

[266] M. Delacre, *Bull. soc chim.* (3), 27, 875-882 (1902); *C. Z.*, 1902, II, 991.

has ceased. The use of the methyl or ethyl ester, or of the free acid yields the same product. When the phenyl ester is used in the reaction, anthracene derivatives are formed.[267] The condensation appeared to be a general one for the preparation of fluorene derivatives. The mechanism of the reaction has not been explained.

Steric hindrance makes impossible the esterification of mesitylene carboxylic acid. It has been found that this hindrance makes difficult the entrance of an alkylated carboxylic group in place of a nuclear hydrogen atom otherwise easily substituted. Thus, mesitylene and methyl or ethyl chlorocarbonate in the presence of aluminum chloride do not condense.[268] On the other hand, the condensation does occur with acid chlorides having an ester substituent. Methyl chloroglyoxylate, $ClOC.COOCH_3$, and mesitylene condense with aluminum chloride to give the methyl ester of mesitylglyoxylic acid. Chlorinated esters do not behave in the same way. The ethyl ester of chloroacetic acid, $ClCH_2COOC_2H_5$, or of iodopropionic acid, $ICH_2CH_2COOC_2H_5$, do not undergo the reaction. There is thus made apparent a great difference in the reactivity of acid chlorides and alkyl halides on one hand, and halogenated esters on the other hand.

When chloromethyl acetate, CH_3COOCH_2Cl, is reacted with mesitylene in the presence of aluminum chloride, the carboxyl group does not enter the nucleus. Instead, dimesitylmethane is obtained in better yields than are secured by condensation of dibromomethane with mesitylene.[269]

As previously stated, chloromethylene dibenzoate, $(C_6H_5COO)_2CHCl$, has been heated with benzene and aluminum chloride to give the benzoate of diphenyl carbinol, $C_6H_5COOCH(C_6H_5)_2$. With mesitylene in benzene solution, however, chloromethylene dibenzoate gives mesityl aldehyde, $(CH_3)_3C_6H_2CHO$. The presence of substituents in the benzene ring appears to prevent addition of the second molecule of hydrocarbon, and to give rise to the aldehyde.[270] Substitution of anisole for mesitylene in the foregoing reaction gave anisaldehyde.

Halogenated Acids and Lactones

Halogenated acids have been reported to condense with aromatic hydrocarbons in the presence of aluminum chloride, with formation of normal substitution products. However, the catalyst often also causes dehydrogenation and the formation of polynuclear products. The formation of fluorene-9-carboxylic acid from trichloroacetic acid and benzene with aluminum chloride is one case of such abnormal procedure.[271]

α,β-Dibromobutyric acid with benzene and aluminum chloride gives α,β-diphenylbutyric acid,

$$CH_3CHBrCHBrCOOH + 2C_6H_6 \xrightarrow{AlCl_3} CH_3CH(C_6H_5)CH(C_6H_5)COOH + 2HBr$$

[267] M. Delacre, *Compt. rend.*, **120**, 155-157 (1895); *J. Chem. Soc. Abs.*, **68** (I), 370 (1895).
[268] F. Wenzel, *Monatsh.*, **35**, 945-952 (1914); *C. A.*, **9**, 599.
[269] F. Wenzel and R. Kugel, *Monatsh.*, **35**, 953-963 (1914); *C. A.*, **9**, 599.
[270] F. Wenzel and L. Bellak, *Monatsh.*, **35**, 965-971 (1914); *C. A.*, **9**, 599.
[271] M. Delacre, *Bull. soc. chim.* (3), **27**, 875 (1902).

However, 9,10-dihydro-9-methyl-phenanthrene-10-carboxylic acid, m p 127°, is also formed during the reaction [272]

Normal condensation products have been obtained from γ-chlorobutyric acid and benzene or toluene, the products being γ-phenylbutyric acid and γ-tolylbutyric acid, respectively [273]

The reaction of 5 2 g of γ,δ-dibromovaleric acid with benzene and 5 2 g of aluminum chloride at 80° for two hours gives 4 2 g of pure γ,δ-diphenylvaleric acid [274]·

$$BrCH_2\ CHBr\ CH_2\ CH_2\ COOH + 2C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2.CH(C_6H_5)\ CH_2\ CH_2\ COOH + 2HBr$$

Aromatically substituted acids have been prepared from chlorolactones of valeric acid and aromatic hydrocarbons Thus δ-chloro-γ-valerolactone with aluminum chloride and benzene at 60-80° yields δ-phenylvaleric acid (m p 57-59°), γ,δ-diphenylvaleric acid (b p 180-182°/0 1 mm), anthracene-9,10-dibutyric acid, and some anthraquinone The main product in the reaction is γ,δ-diphenylvaleric acid, secured in an 80 per cent yield, based on the lactone used [275] The intermediate formation of γ-chloro-δ-phenylvaleric acid is postulated·

$$ClCH_2\ \underset{\underset{O-}{|}}{CH}\ CH_2\ \underset{\underset{---C=O}{|}}{CH_2} \xrightarrow{C_6H_6 + AlCl_3} \left(C_6H_5\ CH_2\ \underset{\underset{Cl}{|}}{CH}\ CH_2CH_2COOH\right)$$

$$\xrightarrow{C_6H_6 + AlCl_3} C_6H_5\ CH_2\ \underset{\underset{C_6H_5}{|}}{CH}(CH_2)_2COOH + HCl$$

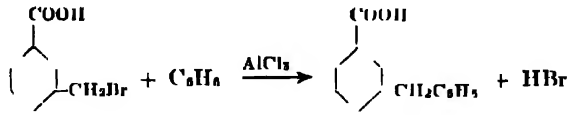
The formation of the polynuclear compounds is due to hydrogenation-dehydrogenation reactions catalyzed by the aluminum chloride The same reaction occurs when toluene is substituted for benzene The tolyl residue is substituted for the chlorine, and there is a complete opening of the lactone ring with intermediate formation of δ-*p*-tolyl-γ-chlorovaleric acid, $(CH_3C_6H_4)\ CH_2\ CHCl\ CH_2\ CH_2\ COOH$ From this with toluene there is formed as the main product, γ,δ-di-*p*-tolyl-valeric acid in a yield of 75 per cent depending on the lactone used [276]

α,α-Bromophenylacetic acid and benzene yields α,α-diphenylacetic acid [277]:

$$\underset{\underset{Br}{|}}{C_6H_5CHCOOH} + C_6H_6 \longrightarrow \underset{\underset{C_6H_5}{|}}{C_6H_5CH\ COOH} + HBr$$

[271] J C Earl and C H Wilson, *J Proc Royal Soc N S Wales*, 65, 178 184 (1932) *C A* 26, 2971
[272] J J Eykman *Chem Weekblad* 4, 727 738 (1907) *J Chem Soc* Abs 94 (1) 22 (1908)
[273] H Beyer, *Ber*, 70, 1101 1113 (1937) *Brit Chem Abstracts* A, 291 (1937)
[274] H Beyer, *Ber* 70, 1101-1113 (1937) *Brit Chem Abstracts*-A, 291 (1937)
[275] H Beyer *Ber*, 70, 1482-1491 (1937) *cf* W Borsche and H Schmidt *Ber*, 72, 1827-33 (1939) *C A*, 34, 719, for Friedel-Crafts react with triarylallylyl chloride, illustrating a case in wh the lactone ring is not broken
[277] J F Eykman, *Chem Weekblad*, 5, 655-666 (1908) *J Chem Soc* Abs 94 (1) 794 (1908)

The condensation of bromo-*m*-toluic acid and benzene with aluminum chloride has been shown to give *m*-benzylbenzoic acid according to the equation:



The yield of *m*-benzylbenzoic acid is 50 per cent of theoretical based on the amount of *m*-toluic acid used (before bromination).[278]

Halogenated Ketones

Halogenated ketones may react with aromatic hydrocarbons with replacement of the halogen by phenyl. When chloroacetophenone is heated with toluene in the presence of aluminum chloride, methyldesoxybenzoin is formed [279]:

$$C_6H_5COCH_2Cl + C_6H_5CH_3 \xrightarrow{AlCl_3} C_6H_5COCH_2C_6H_5 + HCl$$

Likewise, phenylacetone has been obtained in a 32 per cent yield from benzene and chloroacetone [280]:

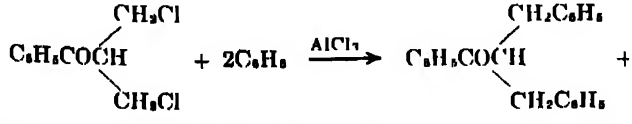
$$ClCH_2COCH_3 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2COCH_3 + HCl$$

Desyl chloride has been found to react readily with benzene in an analogous reaction to give diphenylacetophenone:

$$C_6H_5.CO\ CHCl.C_6H_5 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5.CO\ CH(C_6H_5)_2 + HCl$$

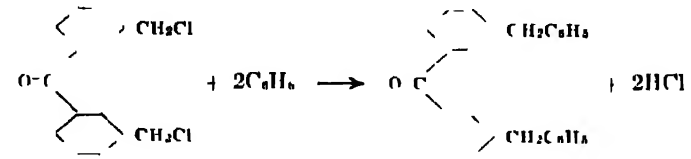
Treatment of 25 g of desyl chloride, in an excess of benzene, with 16 g of aluminum chloride yields 23 g of diphenylacetophenone. Substitution of toluene for benzene likewise gave a good yield of phenyl-*p*-tolylacetophenone. That these condensations are essentially different from ordinary Friedel-Crafts acylations is evident from the fact that molecular equivalents of the catalyst need not be used. The proportion of the catalyst needed, however, is much more than is customarily used in alkylations with alkyl halides.

1,3-Dichloro-2-benzoylpropane has been condensed with benzene, with formation of α,α-dibenzylacetophenone [281]:



[278] P. Senff, *Ann.*, **220**, 247-248 (1883).
[279] A. Collet, *Bull. soc. chim.* (3), **17**, 506-510 (1897).
[280] J. P. Mason and L. I. Terry, *J. Am. Chem. Soc.*, **62**, 1622 (1940).
[281] R. C. Fuson, W. E. Ross, and C. H. McKeever, *J. Am. Chem. Soc.*, **60**, 2935-2936 (1938).

The action of 4,4'-(chloromethyl)benzophenone with benzene in the presence of aluminum chloride gives a quantitative yield of 4,4'-dibenzylbenzophenone [282]



ε-Chloroamylbenzamide reacts with benzene in the presence of aluminum chloride as easily as does amyl chloride. Benzoyl-ε-phenylamylamine is obtained in 90 per cent yield:

$$C_6H_5 \cdot CO \cdot NH(CH_2)_5Cl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5 CO NH(CH_2)_5C_6H_5 + HCl$$

ζ-Chlorohexylbenzamide reacts analogously.[283]

In an investigation of the reversibility of the Friedel-Crafts condensation,[284] it was found that a nuclear halogen is not similarly displaced Thus, in the reaction of β,β-bis(*p*-chlorophenyl)propiophenone with benzene and aluminum chloride, the halogen is not replaced by phenyl Instead, the phenyl group displaces the entire halophenyl radical·

$$(p\text{-}ClC_6H_4)_2CHCH_2COC_6H_5 \xrightarrow{C_6H_6 + HCl + AlCl_3} (C_6H_5)_2CHCH_2COC_6H_5$$

No gas was given off during the reaction; the β,β-diphenylpropiophenone was obtained in 30 per cent yield. That such an exchange is reversible was shown by subjecting α-(benzohydryl)pinacolone to the action of chlorobenzene, aluminum chloride, and hydrogen chloride [285]:

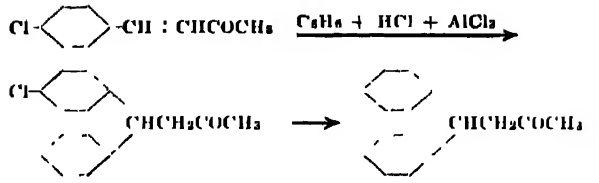
$$(C_6H_5)_2CHCH_2COC(CH_3)_3 \xrightarrow{C_6H_5Cl + HCl + AlCl_3} (p\text{-}ClC_6H_4)_2CHCH_2COC(CH_3)_3$$

The α-(*p,p'*-dichlorobenzohydryl)pinacolone thus obtained may be converted to α-(benzohydryl)pinacolone by treatment with benzene, aluminum chloride, and hydrogen chloride:

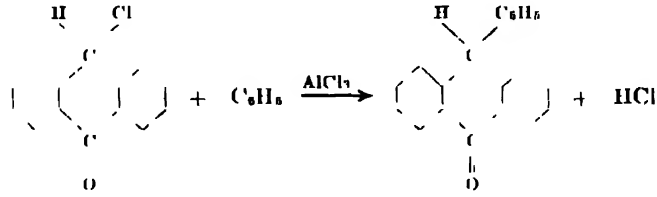
$$(p\text{-}ClC_6H_4)_2CHCH_2COC(CH_3)_3 \xrightarrow{C_6H_6 + HCl + AlCl_3} (C_6H_5)_2CHCH_2COC(CH_3)_3$$

This exchange was also effected in treatment of *p*-chlorobenzalacetone with benzene, aluminum chloride, and hydrogen chloride. Here conversion to benzohydrylacetone takes place according to the scheme [286]:

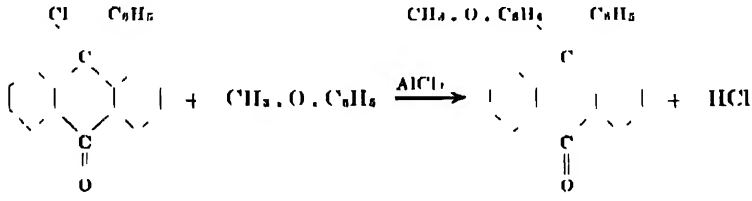
[282] E. Comenade *Bull soc. chim. Belg.*, 44, 411-424 (1935) *C. A.*, 30, 1373
[283] J. v. Braun, *Ber.* 43, 2837-2852 (1910) *C. A.*, 4, 488-490
[284] J. T. Eaton, D. B. Black and R. C. Fuson, *J. Am. Chem. Soc.*, 56, 687-688 (1934)
[285] H. Weinstock and R. C. Fuson *J. Am. Chem. Soc.*, 56, 1241-1242 (1934)
[286] C. F. Woodward, G. T. Borcherdt, and R. C. Fuson, *J. Am. Chem. Soc.*, 56, 2103-2105 (1934)



Halogenated anthrones condense with aromatic hydrocarbons or ethers in the presence of aluminum chloride with replacement of halogen. With aromatic hydrocarbons the condensation proceeds [287]:



Treatment of chlorophenylanthrone with anisole and aluminum chloride in carbon disulfide solution gives anisylphenylanthrone:



Similar condensation occurs when phenetole or dimethylaniline is substituted for anisole in the preceding reaction.[288]

Halogenated Ethers

Replacement of halogen by Friedel-Crafts condensation of chloroethers with aromatic hydrocarbons does not proceed readily. Several instances cited in the literature illustrate the difficulties encountered in this type of reaction.

Verley [289] has reported that reaction of 1 mole of chloromethyl ethyl ether with 1 mole of benzene in the presence of 1 mole of aluminum chloride proceeds with the formation of diphenylmethane in almost theoretical yield. He assumed the intermediate formation of benzyl ethyl ether, reaction of the ether with hydrogen chloride with formation of benzyl chloride, and subsequent formation of diphenylmethane by reaction of the benzyl chloride with benzene:

[287] E. Barnett and J. W. Cook, *J. Chem. Soc.*, 123, 2631-2642 (1923), see also section of this book dealing with replacement of nuclear halogen.
[288] L. Tetry, *Compt. rend.*, 128, 1406-1407 (1899); *J. Chem. Soc. Abs.*, 76 (1), 818 (1899).
[289] A. Verley, *Bull. soc. chim.* (3), 17, 908-914 (1897); *C. Z.*, 1897, II, 1173

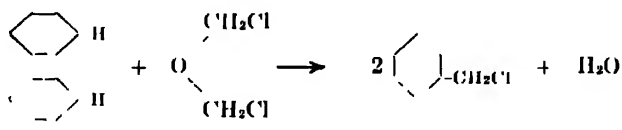
(1) $ClCH_2.O.C_2H_5 \xrightarrow{AlCl_3 + C_6H_6} C_6H_5CH_2.O.C_2H_5 + HCl$

(2) $C_6H_5CH_2.O.C_2H_5 + HCl \longrightarrow C_6H_5CH_2Cl + C_2H_5OH$

(3) $C_6H_5CH_2Cl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5 + HCl$

The work was repeated by Huston and Friedemann [290] who were not able to confirm the formation of benzyl ethyl ether during the reaction. Although the aluminum chloride was added slowly to a well-cooled mixture of chloromethyl ethyl ether and benzene, the temperature rose to 43° during the reaction. The products were diphenylmethane and anthracene. These workers suggested that the condensation may proceed through primary decomposition of the chloromethyl ethyl ether into formaldehyde, and subsequent reaction of the formaldehyde with benzene to yield diphenylmethane and anthracene.

Such an explanation, however, brings up a question concerning the mechanism of the reaction of formaldehyde with aromatic hydrocarbons. Diphenylmethane and anthracene are produced upon treatment of formaldehyde with benzene and aluminum chloride. It has been suggested, however, that benzyl chloride, probably an intermediate product in this formation of diphenylmethane, is produced by reaction of dichlorodimethyl ether and benzene.[291]



Since the course of the reaction of formaldehyde with benzene and aluminum chloride has not yet been definitely shown,[292] the production of diphenylmethane from chloromethyl ethers and benzene cannot be ascribed to preliminary decomposition of the halogenated ether to formaldehyde.

The condensation of aromatic hydrocarbons with hydrogen chloride and formaldehyde in the presence of Friedel-Crafts type catalysts is an accepted method for the preparation of chloromethyl derivatives.[293] Benzene with formaldehyde and hydrogen chloride thus yield benzyl chloride.[294] A study of this reaction might elucidate the mechanism of Friedel-Crafts condensations with chloro-ethers.

According to Sommelet [295] carbon disulfide solutions of chloromethyl methyl ether, chloromethyl ethyl ether, or chloromethyl propyl ether, when mixed with benzene in the presence of aluminum chloride, at or

[290] R. C. Huston and T. E. Friedemann *J. Am. Chem. Soc.*, **38**, 2527-2533 (1916).

[291] F. M. Litterscheid *Inn.*, **316**, 189 (1901).

[292] *cf.* G. B. Frankforter and V. Kokatnur, *J. Am. Chem. Soc.*, **37**, 2399-2401 (1915). R. C. Huston and D. T. Ewing, *J. Am. Chem. Soc.*, **37**, 2401 (1915).

[293] *cf.* L. F. Fieser and D. K. Snow *J. Am. Chem. Soc.*, **60**, 176-177 (1938).

[294] G. Blanc, *Am. Parfumer*, **17**, 541-542; *C. A.*, **17**, 1630; *Bull. soc. chim.*, **33**, 313-319 (1923).

[295] M. Sommelet, *Compt. rend.*, **157**, 1443-1445 (1913); *C. A.*, **8**, 1086.

below 0°, form the corresponding ethers together with varying amounts of benzyl chloride, two concurrent reactions taking place:

$$(1)\quad C_6H_6 + ClCH_2.O.R \xrightarrow{AlCl_3} C_6H_5.CH_2.O.R + HCl$$

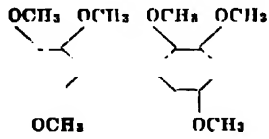
$$(2)\quad C_6H_6 + R.O.CH_2Cl \longrightarrow C_6H_5CH_2Cl + ROH$$

In this way a 30 per cent yield of benzyl propyl ether from benzene and chloromethyl propyl ether was secured. Addition of a little tin tetrachloride catalyst causes exclusive formation of benzyl chloride. Benzene homologs—toluene, *o*, *m*, and *p*-xylene, mesitylene, isopropylbenzene, and cymene—were shown to react analogously.

von Braun [206] reacted γ-chloropropyl phenyl ether with an equivalent amount by weight of aluminum chloride in 10 parts of benzene. He obtained only a very small yield of γ-phenylpropyl phenyl ether; varying reaction conditions did not improve the yield. The reaction was shown to proceed in like manner with ε-chloroamyl phenyl ether; ε-phenylamyl phenyl ether was secured in only a very low yield. The main reaction product (6 g from 20 g of the chloro-ether) had the composition $C_6H_5.C_5H_9$. Its structure was not determined.

Condensation of α,β-dichloroethyl ether, $CH_2Cl.CHCl.O.C_2H_5$, and benzene with aluminum chloride has likewise been reported to proceed in complex fashion. No normal substitution product was isolated; instead, the reaction products consisted of toluene, ethylbenzene, diphenylmethane, bibenzyl, and anthracene.[207]

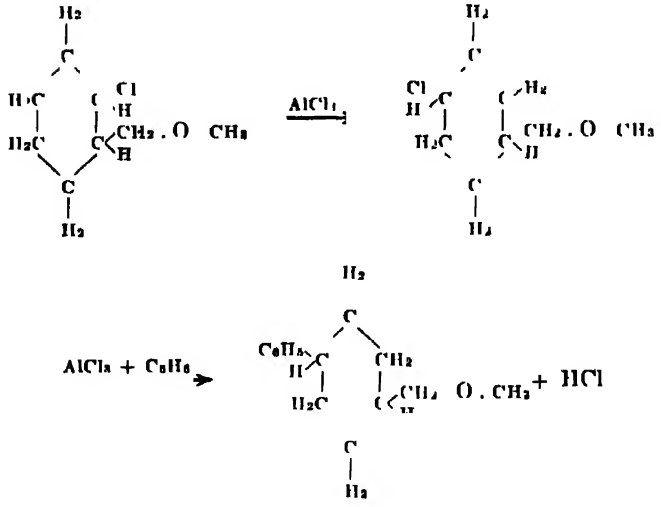
Treatment of a halogenated trimethoxybenzene with aluminum chloride has been shown to result in the formation of a biphenyl derivative. 5-Bromo-1,2,4-trimethoxybenzene treated with an equivalent amount by weight of aluminum chloride in ether or nitrobenzene solution after twenty hours gives 2,3,5,2′,3′,5′-hexamethoxybiphenyl [208]:



Cleavage and migration of the halogen must have occurred during the reaction, with subsequent condensation of the rearranged halogen compound with the dehalogenated product.

Halogen migration has been observed during the aluminum chloride condensation of 1-(methoxymethyl)-2-chlorocyclohexane and benzene, with formation of 1-(methoxymethyl)-4-phenylcyclohexane [209]:

[206] J. von Braun, *Ber.*, **43**, 2837-2852 (1910); *C. A.*, **4**, 488-490 (1910).
[207] A. Gardeur, *Bull. Acad. roy. Belgique. (3)*, **34**, 930-933; *C. Z.*, 1898, I, 438.
[208] W. Baker and C. Evans, *J. Chem. Soc.*, 372-375 (1938).
[209] C. D. Nenitzescu and V. Przemetski, *Ber.*, **69**, 2706-2707 (1936).



Halogenated Aldehydes

The course of the reaction of halogen-substituted aldehydes with aromatic hydrocarbons depends upon the reaction conditions employed It may proceed as

(1) A Friedel-Crafts condensation, with replacement of halogen,
(2) An aldol condensation, with formation of a halogenated alcohol;
(3) A Baeyer reaction, with formation of halogenated hydrocarbons

Friedel-Crafts replacement has been reported only by earlier workers Only isolated instances of aldol condensations have been cited The greater part of the work which has been done deals with an investigation of Baeyer condensations effected by reaction of trihalogenated aldehydes with aromatic compounds in the presence of aluminum chloride

Investigators citing replacement of halogen by reaction of chloral with benzene note the formation of several products. Upon adding aluminum chloride to chloral with an excess of benzene, Combes [300] reported that he isolated four substances:

diphenylchloral hydrochloride,
diphenyldichloroethane,
a solid compound, $C_{22}H_{17}Cl$, m p. 83°,
tetraphenylethane.

Repetition of the work by Biltz [301] led to the production of a heavy oil, b_{12} 160-165°. He also secured by-products which were not separable by fractionation and which could be removed entirely from the fraction b_{12} 160-165°. Biltz varied the method of procedure by adding a solution of chloral in benzene to a mixture of aluminum chloride and benzene Here he obtained small quantities of tetraphenylethane and some tri-

[300] A Combes *Compt rend*, **98**, 678 (1884)
[301] H Biltz, *Ber*, **26**, 1952-1960 (1893) *J Chem Soc Abs*, **64** (I), 718 (1893)

phenylmethane. After much research, the following was found to be the best method of procedure. To a mixture of 1000 g of benzene, 300 g of carbon disulfide, and 60 g of chloral heated to 60°C, was gradually added 60 g of aluminum chloride in small portions of 3 to 5 g. After adding about a third of the aluminum chloride, the flask was heated under reflux for fifteen minutes on the water-bath, whereby strong evolution of hydrogen chloride began. The remainder of the aluminum chloride was added in the period of one hour, and the reaction mixture was heated for another hour. The dark brown mass which appeared was removed in a separatory funnel and washed. Upon standing overnight, about 15 g of yellow crystals, consisting essentially of tetraphenylethane, appeared. By fractionation of the mother liquor, there was obtained from the fraction b. 200-340° a compound m. 80° which was found to be diphenyldichloroethylene; and from the fraction b. 340-355°, a compound m. 136°, identified as triphenylvinyl alcohol. From the fraction b 355-400° there was obtained a small amount of a hydrocarbon, m. 232-233°, which was converted by oxidation into a substance which melts at 166-167°.

A further investigation [302] of the products of the reaction of benzene with chloral showed that the following were formed:

tetraphenylethane, $CH.(C_6H_5)_2.CH(C_6H_5)_2$, m 211°, b. 379-383°
diphenyldichloroethylene, $C(C_6H_5)_2CCl_2$, m. 80°, b. 336°
triphenylvinyl alcohol, $C(C_6H_5)_2{:}CC_6H_5.OH$, m. 136°.

The mother liquors accumulated during this investigation were found to contain

phenyldichloroethylene
diphenylmethane
triphenylmethane

The hydrocarbon melting at 232-233° was found to be 9,10-diphenylphenanthrene.[303] The same compound is obtained by the action of aluminum chloride on a benzene solution of tetraphenylethylene.

Böeseken [304] reported that the action of chloral and aluminum chloride on benzene yielded diphenylmethane. In order to elucidate the mechanism of the reaction he investigated the dissociating action of aluminum chloride on chloral.

An aldol condensation with subsequent cleavage of hydrogen halide has been reported [305] to occur in the condensation of polymeric bromoisobutyraldehyde with benzene and aluminum chloride in carbon disulfide solution. The cyclic, trimeric bromoisobutyraldehyde thus gave a 70 per cent yield of phenyl isopropyl ketone. The condensation was thought to proceed through primary depolymerization of the aldehyde, and subsequent addition of benzene with formation of a secondary alcohol:

$$(CH_3)_2CBr.CHO + C_6H_6 \longrightarrow (CH_3)_2CBr.CH(OH).C_6H_5$$

[302] H. Biltz, *Ann.*, **296**, 219-260 (1897); *J. Chem. Soc. Abs.*, 533 (1897).
[303] H. Biltz, *Ber.*, **38**, 203-206 (1905); *J. Chem. Soc. Abs.*, **88** (I), 188 (1905).
[304] J. Böeseken, *Rec. trav. chim.*, **30**, 381-391 (1911); *C. Z.*, 1912, I, 897.
[305] A. Franke and A. Klein, *Monatsh.*, **33**, 1233-1242 (1912); *C. Z.*, 1913, I, 1004.

This was later assumed to crack off HBr to give an unsaturated alcohol:

$$(CH_3)_2CBr.CH(OH)\,C_6H_5 \longrightarrow (CH_3)_2C{:}\,C(OH).C_6H_5$$

Rearrangement of the unsaturated alcohol gave phenylisopropyl ketone:

$$(CH_3)_2C : C(OH) . C_6H_5 \longrightarrow (CH_3)_2CH . \underset{\displaystyle C_6H_5}{\overset{\displaystyle O}{\overset{\|}{C}}}$$

An 80 per cent yield of trichloromethylphenyl carbinol, $C_6H_5.CHOH.CCl_3$, m. 37°, was obtained by Dinesmann [306] when he treated 1000 g of benzene with 200 g of chloral and 40 g of aluminum chloride in the cold during a period of three hours. The reaction was expressed as follows:

$$C_6H_6 + OCH\,CCl_3 \cdot \qquad C_6H_5(OH)CH\,CCl_3$$

The aldol condensation thus obtained could not be duplicated by Frankforter and Kritchevsky.[307] Using 2 moles of benzene instead of the large excess employed by Dinesmann, and keeping the temperature at 0°, they obtained simple condensation instead of the aldol reaction. The aluminum chloride served as a dehydrating agent, according to the reaction:

$$2C_6H_6 + OCH.CCl_3 + Al_2Cl_6 \qquad (C_6H_5)_2CHCCl_3 + H_2O + Al_2Cl_6$$

By adding 300 g of chloral and 175 g of aluminum chloride to 300 g of toluene, *p*-ditolyltrichloroethane, $(CH_3.C_6H_4)_2CHCCl_3$, m.p. 88°, was obtained. In preparing this compound, an oil was also secured which was found to be *p*-tolyldichloroacetaldehyde hydrochloride, $CH_3.C_6H_4.CCl_2CHO.HCl$.

By adding 98 g of chloral and 80 g of aluminum chloride to 100 g of xylene, Frankforter and Kritchevsky prepared di-*m*-xylyltrichloroethane. No other substance was formed, the only reaction taking place being one of simple condensation. Using the same procedure, cymene was reacted with chloral and aluminum chloride, but no definite product could be isolated.

The action of chloral and bromal with polycyclic hydrocarbons and aluminum chloride proceeds as it does with benzene homologs, forming analogous Baeyer-reaction condensation products.[308] The reaction with naphthalene is so energetic that if great care is not observed total decomposition occurs. At 0° or below, the condensation is almost quantitative. Anthracene and phenanthrene react similarly. The product obtained in each case depends on the solvent used. Thus, from anthracene, chloral, and aluminum chloride the following products are obtained when the indicated solvents are used:

Solvent	Product
carbon disulfide	9,10-anthracene-trichloroethane
benzene	9,10-anthracene-dichloroethylene
petroleum ether	dianthracene-dichloroethylene

[306] A. Dinesmann, *Compt. rend.*, 141, 201-203 (1905); *C. Z.*, 1905, II, 753.
[307] G. B. Frankforter and W. Kritchevsky, *J. Am. Chem. Soc.*, 36, 1511-1540; *C. A.*, 8, 3795.
[308] G. B. Frankforter and W. Kritchevsky, *J. Am. Chem. Soc.*, 37, 385-392 (1915).

The condensation of chloral with alcohol and aluminum chloride has been reported to yield a compound having the general physical properties of trichloroacetal. With benzyl alcohol the reaction product was a chloro-compound giving the aldehyde reaction, but a substance with a constant boiling point could not be isolated. With phenol a compound, m. 212°, possibly *p*-dihydroxydiphenyltrichloroethane, was prepared. When resorcinol and chloral in carbon disulfide were treated with aluminum chloride, diresorcyldichloroethylene was the reaction product.[309]

Aluminum chloride reacts vigorously at ordinary temperatures with phenol ethers in the presence of chloral and bromal, but if the temperature is kept below 0°, the reaction gives a quantitative yield of the same condensation products as are formed with the use of concentrated sulfuric acid.[308]

In an extensive investigation of the action of halogen-substituted aldehydes, alcoholates, and acetals on aromatic hydrocarbons and ethers in the presence of aluminum chloride at 0°, Harris and Frankforter[310] concluded that condensation proceeded as the Baeyer reaction, and that quantitative yields of condensation products could be obtained. The following reactions were studied: chloral with benzene, toluene, anisole, phenetole, cresol methyl ether, and *p*-cresol ethyl ether; bromal with the foregoing aromatic compounds; dibromoacetaldehyde with anisole, phenetole, *p*-cresol methyl ether, and *p*-cresol ethyl ether; bromoacetal with anisole and phenetole; and chloral alcoholate with phenetole.

The condensation of acids with chloral and aluminum chloride has also been studied.[311] Chloral was found to combine with acetic acid or other monobasic acids with the formation of, for instance, $Al_2Cl(OOCCH_3)_5$·CCl_3CHO. Benzoic acid was found not to react with chloral and aluminum chloride.

The condensation of benzene with chloral hydrate, $CCl_3CHO.H_2O$, in the presence of aluminum chloride also proceeds with the formation of halogenated compounds. Trichlorodiphenylethane, $CCl_3.CH(C_6H_5)_2$, obtained as one of the products, apparently undergoes partial condensation, giving a resin. At the same time some of the trichlorodiphenylethane condenses with more C_6H_6 to give 1-chloro-1,1,2,2-tetraphenylethane.[312]

In order to elucidate the reactions of chloral, bromal, and chloral hydrate with certain aromatic compounds, a series of studies on the action of paraformaldehyde with aromatic hydrocarbons in the presence of aluminum chloride has been undertaken.[313] The diverse results obtained in these investigations, however, do not tend to clarify the

[309] G. B. Frankforter and W. Kritchevsky, *Orig. Com. 8th Inter. Congr. Appl. Chem. (Appendix)*, 25, 361; *C. A.*, 7, 2188 (1913).

[310] L. E. Harris and G. B. Frankforter, *J. Am. Chem. Soc.*, 48, 3144-3150 (1926).

[311] G. B. Frankforter and W. Kritchevsky, *J. Am. Chem. Soc.*, 36, 1511-1549 (1914); *C.*, 1, 3795.

[312] M. van Laer, *Bull. soc. chim. Belg.*, 28, 346-350 (1919); *C. A.*, 16, 2136.

[313] G. B. Frankforter and V. Kokatnur, *J. Am. Chem. Soc.*, 37, 2399-2401 (1915); 36, 1529-1537 (1914). R. C. Huston and D. T. Ewing, *J. Am. Chem. Soc.*, 37, 2391-2399, 2401 (1915).

mechanism of aluminum chloride-catalyzed condensations with halogenated aldehydes.*

Nitrogenous Halides

The introduction of aryl groups by the Friedel-Crafts reaction into nitrogenous compounds containing replaceable halogen offers a valuable tool for the manufacture of many products of industrial importance. A discussion of such reactions with the following nitrogen-containing halides is here given:

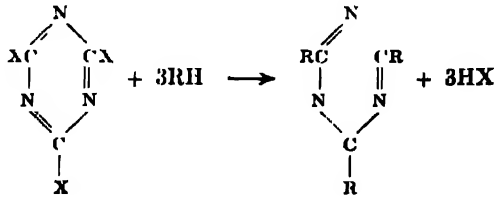
Cyanogen halides
Cyanuric halides
Halogenated amides and imides
Diazonium halides
Halogen salts of amines
Halogenated nitro- compounds
Halogenated ring compounds of nitrogen

Acylations in which the reactive agents are nitrogenous carboxylic acid chlorides or compounds leading to intermediate production of such acid chlorides, *e.g.*, cyanates or isocyanates with hydrogen chloride, are not included here.** Gattermann's aldehyde synthesis, based on the use of hydrogen cyanide and hydrogen chloride, is also reserved for special treatment.†

Cyanogen Halides.—The reaction of freshly prepared cyanogen halides with aromatic compounds yields the corresponding nitriles:

$$CNX + RH \longrightarrow RCN + HX$$

Unless the cyanogen halide is freshly prepared or is in the nascent state, it reacts in its polymeric form as cyanuryl chloride, to give substituted cyclic triazines:

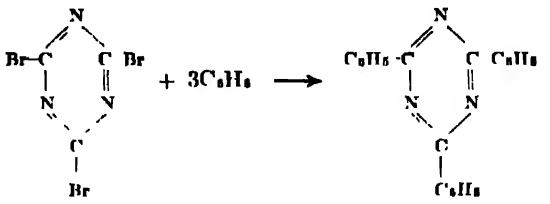


Early investigators[314] have noted that cyanogen halides act also as halogenating agents. This is especially noticeable with the iodides, which give iodo-compounds almost exclusively.[315]

Scholl and his co-workers[316] reported that cyanogen bromide with

* See Chapter 12.
** For condensations of this type see Chapter 6
† See Chapter 10.
[314] C. Friedel and J. M. Crafts, *Ann. chim. phys (6)*, 1, 528 (1884). O. Folin, *Am. Chem. J.*, 19, 323-352 (1897); *C. Z.*, 1897, II, 23
[315] cf. P. Karrer, A. Rebmann, and F. Zeller, *Helv. Chim. Acta*, 3, 261-272 (1920).
[316] R. Scholl and W. Norr, *Ber.*, 33, 1052-1058 (1900). R. Scholl and R. Kacer, *Ber.*, 36, 322-331 (1903). R. Scholl, *Ber.*, 36, 10-15 (1903).

aromatic hydrocarbons in the presence of aluminum chloride gives only traces of nitriles. With benzene and cyanogen bromide at 50° they secured considerable quantities of cyaphenine, probably resulting from the action of benzene on cyanuric bromide:



Nitriles likewise could not be obtained from toluene, the xylenes, or *p*-cymene. With anisole, however, the product for the most part consisted of anisonitrile and *p*-bromoanisole. This may be accounted for by the greater reactivity of anisole over that of the aromatic hydrocarbons. Condensation occurred before the cyanogen bromide had polymerized.

More recently, Karrer and Zeller [317] found that good yields of nitriles may be obtained when aromatic hydrocarbons are mixed with finely powdered aluminum chloride and freshly prepared cyanogen bromide and subsequently warmed until evolution of halogen bromide ceases. Unless the cyanogen bromide is freshly prepared, the reaction leads to negative results because of polymerization of the halide. Karrer and Zeller obtained 10 g of benzonitrile by adding 15 g of cyanogen bromide to 25 g of aluminum chloride suspended in 150 cc of benzene. Nitriles were also prepared from toluene and from anthracene.

Subsequent investigation [318] of the range of applicability of this method showed that the reaction could be used for the synthesis of 3-cyanoacenaphthene and cyanothiophene [319] in excellent yields, but that less satisfactory results are secured with *m*-methyl-*tert*-butylbenzene and with naphthalene, which yield a mixture of cyano- derivatives. No condensation occurred with acenaphthene, indene, and biphenyl. Best results were obtained with phenol ethers, the following nitriles being prepared from the corresponding ethers:

2,4-dimethoxybenzonitrile
2,5-dimethoxybenzonitrile
3,4-dimethoxybenzonitrile
2,3,4-trimethoxybenzonitrile
4-ethoxynaphthonitrile
2-methoxynaphthonitrile

Small amounts of hydroxy nitriles were usually formed as by-products in the reaction with ethers, due to hydrolysis of the alkoxy- groups by the

[317] P. Karrer and E. Zeller, *Helv. Chim. Acta*, **2**, 482-486 (1919); *C. A.*, **14**, 743.
[318] P. Karrer, A. Rebmann, and E. Zeller, *Helv. Chim. Acta*, **3**, 261-272 (1920); *J. Chem. Soc. Abs.*, **118** (I), 389 (1920).
[319] For subsequent work on the condensation of thiophene with cyanogen halides, see W. Steinkopf, *Ann.*, **430**, 87-90 (1923).

catalyst. The condensation could not be effected with biphenyl and anthranol methyl ethers.

Cyanogen chloride was found to give the same products as the bromide, and was almost equally reactive. Cyanogen iodide, however, was found to be less useful.

Of interest in this connection is some early work dealing with the production of nitriles by reaction of aluminum chloride and mercury fulminate on aromatic hydrocarbons or phenol ethers. Nascent cyanogen chloride produced during the course of the reaction resulted in the production of nitriles in good yield.

This condensation has been reported by Scholl [320] to proceed with production of either aromatic nitriles or aromatic aldoximes, depending on the purity of the catalyst. Scholl added mercury fulminate to a mixture of benzene and aluminum chloride, and assumed that the reaction proceeded through primary formation of fulminic acid by the action of hydrogen chloride on the fulminate, subsequent formation of cyanogen chloride by the action of the catalyst on fulminic acid, and final condensation of cyanogen chloride with the hydrocarbon:

$$C:NOH \xrightarrow{AlCl_3} C:NCl \longrightarrow Cl.C:N \xrightarrow{C_6H_6} C_6H_5CN$$

In this way an 80 per cent theoretical yield of benzonitrile was obtained. The condensation proceeds even more smoothly with benzene homologs. If the catalyst is not absolutely anhydrous, however, and is not present in excess, aldoximes are formed:

$$C_6H_6 + C:NOH \xrightarrow{Al_2OCl_4} C_6H_5.CH:NOH$$

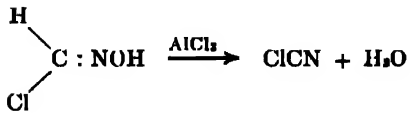
As aluminum chloride does not convert benzaldoxime into benzonitrile either in boiling benzene or carbon disulfide solution, Scholl stated that the formation of a nitrile in this synthesis cannot be due merely to the dehydrating action of dry aluminum chloride on an oxime already formed.

According to Nef [321] the action of hydrogen chloride on mercury fulminate and sodium fulminate results in the formation of formylchloride oxime:

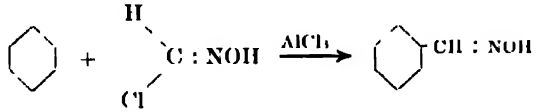
$$\begin{matrix} H \\ \diagdown \\ \quad C:NOHg \\ \diagup \\ Cl \end{matrix} + HCl \longrightarrow \begin{matrix} H \\ \diagdown \\ \quad C:NOH \\ \diagup \\ Cl \end{matrix} + HgCl$$

Böeseken [322] has suggested that perhaps the condensation of mercury fulminate and benzene with aluminum chloride proceeds through primary formation of Nef's oxime, which is easily dehydrated by the action of aluminum chloride to cyanogen chloride:

[320] R. Scholl, *Ber.*, 32, 3492-3501 (1899). R. Scholl and W. Norr, *loc. cit.* R. Scholl and F. Karr, *loc. cit.* R. Scholl, *Ber.*, 36, 10-15 (1903). R. Scholl, *Chem. Ztg.*, 24 (1), 15 (1900).
[321] J. U. Nef, *Ann.*, 280, 3017 (1894).
[322] J. Böeseken, *Rec. trav. chim.*, 24, 8-18 (1905).



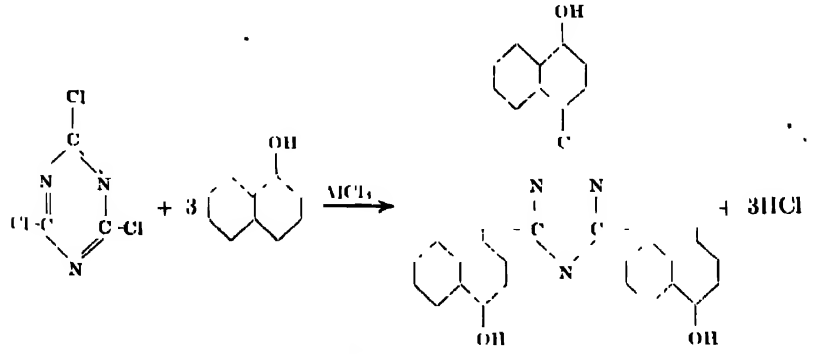
The condensation would then proceed normally, with formation of nitrile. If the catalyst were not present in sufficient strength to effect dehydration of the primarily formed oxime, the reaction would yield the aldoximes secured by Scholl:



The condensation of polymeric cyanogen halides (cyanuric halides) with benzene and aluminum chloride to give cyaphenine had been noted by Scholl and Norr.[320] Since then the condensation of cyanuric halides with aromatic hydrocarbons has been applied to products of industrial interest. Benzoic acid in 83-96 per cent yields is claimed to be formed by heating molecular equivalents of benzene, cyanuryl chloride, and aluminum chloride under reflux, and subsequently hydrolyzing the cyaphenine obtained.[323]

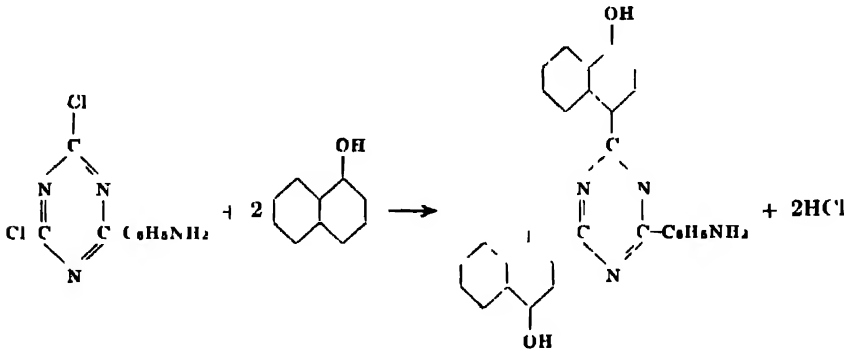
The condensation products of a cyanuric halide with one to three moles of a polynuclear aromatic compound in the presence of aluminum chloride yields dyes which may be used to color solid or liquid hydrocarbons. The aromatic component may be phenanthrene, chrysene, N-ethylcarbazole, pyrene, or perylene.[324]

Dyestuff intermediates are obtained by condensation of chlorinated triazines with α-naphthol in the presence of aluminum chloride.[325] Cyanuric chloride with α-naphthol yields 2,4,6-tris(4′-hydroxynaphthyl)1,3,5-triazine:



[320] U. S. P. 1,734,029 (1929) to G. Barsky and I. V. Giles (to American Cyanamid Co.); *C. Z.*, 1930, I, 740; *Brit. Chem. Abstracts-B*, 8 (1930).
[323] Brit. P. 480,604 (1936) to A. Carpmael (to I. G. Farbenindustrie); *Brit. Chem. Abstracts-A*, 183 (1938).
[324] Swiss P. 108,191-108,202 (1924); Brit. P. 220,302 (1923), French P. 584,043 (1923) to Soc. f. chem. Ind. in Basel. *C. Z.*, 1925, II, 780-781.

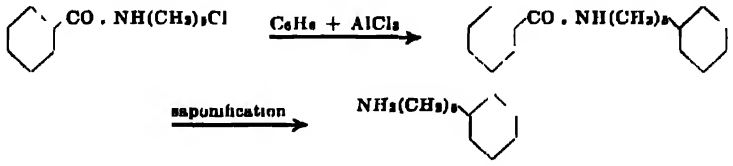
Mono- or di-chlorinated triazines may be used. 2-Phenylamino-4,6-dichloro-1,3,5-triazine (the condensation product of cyanuric chloride with 1 mole of aniline) and α-naphthol yields 2-phenylamino-4,6-bis(4'-hydroxynaphthyl)-1,3,5-triazine:



One of two of the chlorine atoms of cyanuryl chloride may be replaced by any aliphatic or aromatic group, and the resulting compound condensed with α-naphthol.

α-Naphthol in the above condensations may be replaced by other phenols or by phenol ethers or by a mixture of such constituents.[326]

Halogenated Amides and Imides.—Benzamides with an N-alkyl halide substituent easily undergo Friedel-Crafts reaction, with replacement of halogen.[327] Since saponification of the reaction products yields amines, the condensation affords a good method for the preparation of aralkylamines. ε-Phenylamylamine is obtained from N-ε-chloroamylbenzamide and benzene:



ζ-Chlorohexylbenzamide has been similarly condensed.

The reaction proceeds equally well with toluene or *p*-xylene instead of benzene. N-ε-Chloroamylbenzamide is dissolved in 10 times the amount by weight of toluene, and treated with an equivalent amount by weight of aluminum chloride. The reaction mixture is heated for four hours on the water-bath, the solvent removed, and the residue fractionated to give an oil, b.p. 265-270°. Saponification of this product with concentrated hydrochloric acid yields ε-*p*-tolylamylamine:

[326] German P. 433,100 (1926), Brit. P. 240,371 (1925) to Soc. f. chem. Ind. in Basel; *C. Z.*, 1926, II. 2117.

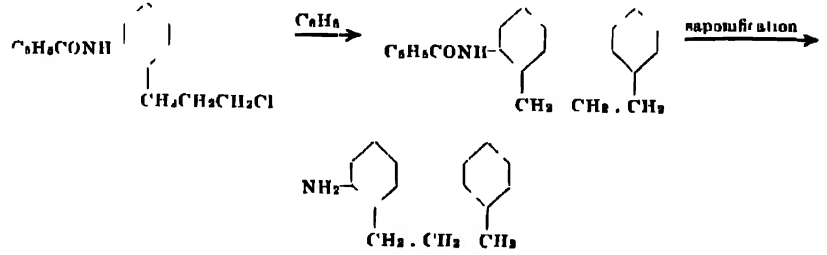
[327] J. v. Braun, *Ber.*, 43, 2857-2862 (1910); see Chapter 6 for reaction of carbamyl chloride (chloroformamide) and its derivatives with aromatic compounds.

$$C_6H_5 . CO . NH(CH_2)_3Cl + C_6H_5 \cdot CH_3 \xrightarrow{AlCl_3}$$

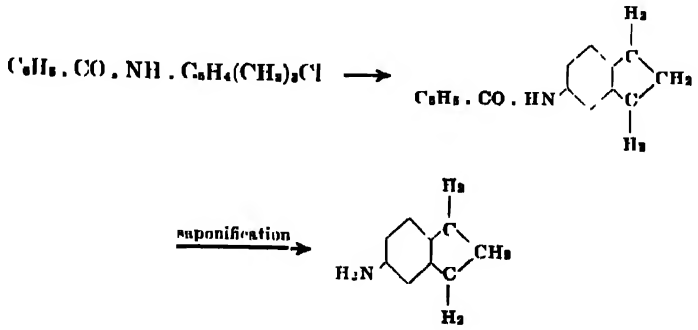
$$C_6H_5 \cdot CO . NH(CH_2)_3 . C_6H_3 \cdot CH_3 \xrightarrow{\text{saponification}}$$
$$NH_2 . (CH_2)_3 \cdot C_6H_3 . CH_3 .$$

Condensation with xylene proceeds likewise to give a 90 per cent yield of the benzoyl derivative of ε-*p*-xylyl-*n*-amylamine, which is easily saponified to ε-*p*-xylyl-*n*-amylamine.[328]

The *o*-benzamido derivative of γ-phenylpropyl chloride also condenses very easily with aromatic compounds. Amino-diaryl derivatives of propane may be obtained[320] according to the scheme:



4-Benzoylaminobibenzyl, m.p. 170-171°, is obtained in almost theoretical yield by the condensation of *p*-benzoylaminophenylethyl chloride with benzene in the presence of aluminum chloride. In the reaction of *p*-benzoylaminophenylpropyl chloride with benzene and aluminum chloride, an oily product is obtained. Upon hydrolysis with hydrochloric acid, *p*-aminodiphenylpropane is secured as the main product, together with a colorless mobile base, b.p. 95-110°/17 mm, which is probably aminohydrindene, formed by intramolecular ring closure[330]:



Benzanilidimido chlorides condense with dialkyanilines in the presence of aluminum chloride in carbon disulfide wtih replacement of halogen

[328] J. v. Braun and M. Kuhn, *Ber.*, 60, 2557-2566 (1927); *C. A.*, 22, 1146.
[329] J. v. Braun and H. Deutsch, *Ber.*, 45, 2171-2183 (1912); *C. A.*, 6, 2027
[330] J. v. Braun, H. Deutsch, and O. Kruczelski, *Ber.*, 46, 1511-1526 (1913); *J. Chem. Soc. Abs.*, 104 (I) 770 (1913).

to give substitution products which are easily hydrolyzed to the corresponding ketones [331]:

$$C_6H_5 . CCl : N . C_6H_5 + C_6H_5N(CH_3)_2$$
$$C_6H_5 . C(:N . C_6H_5) . C_6H_4 . N . (CH_3)_2 \xrightarrow{H_2O} C_6H_5 . CO . C_6H_4N(CH_3)_2$$

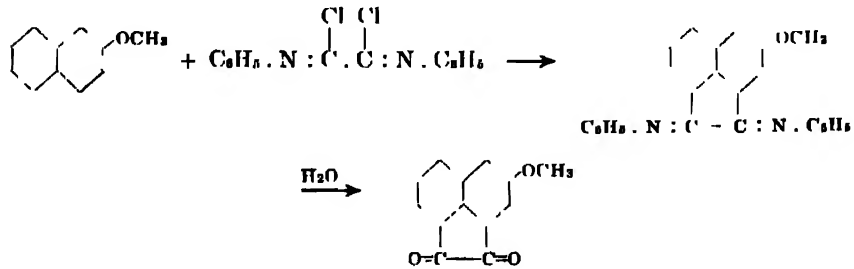
In this way benzanilidimido chloride was condensed with dimethyl aniline to give an 80 per cent yield of dimethylaminobenzophenone. Diethylaminobenzophenone was similarly secured in 70 per cent yield.

The condensation may likewise be effected with *p*-bromo- or *p*-nitrobenzanilidimido chloride. With these reactants the following ketones were obtained in the indicated yields:

4′-nitro-4-dimethylaminobenzophenone	50%
4′-nitro-4-diethylaminobenzophenone	50%
4′-bromo-4-dimethylaminobenzophenone	70%

The substitution of dry ether for carbon disulfide in the process results in smoother reaction [332] Using this solvent, ready condensation of benzanilidimido chloride was secured with dimethyl-*o*-, -*m*-, and *p*-toluidine, diethyl-*o*-toluidine, dimethyl-α-naphthylamine, benzylmethylanilme, and benzylethylaniline Upon hydrolysis the corresponding ketones were secured.

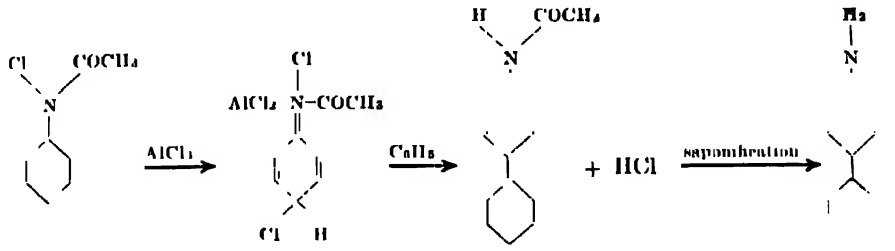
Staudinger and co-workers [333] attempted the preparation of diketones by reaction of diphenylmido chlorides with aromatic hydrocarbons or phenol ethers in the presence of aluminum chloride. Brown, amorphous decomposition products were formed in nearly all condensations tried. With the methyl and ethyl ethers of β-naphthol, however, the corresponding acenaphthenequinones were obtained in 75 and 44 per cent yields, respectively, the condensations proceeding:



The condensation of N-haloacyl derivatives of amino- compounds of the benzene series with aromatic hydrocarbons in the presence of aluminum chloride, and subsequent saponification of the products obtained,

[331] R. C. Shah and J. S. Chaubal, *J. Chem. Soc.*, 650 (1932).
[332] R. C. Shah and M. B. Ichapora, *J. Chem. Soc.*, 894-896 (1935).
[333] H. Staudinger, H. Goldstein, and E. Schlenker, *Helv. Chim. Acta*, 4, 342-364 (1921); *C. A.*, 15, 3446.

results in the formation of amino-biphenyl derivatives in 70 per cent yields.[334] Migration of halogen is assumed in the reaction of N-chloroacetanilide with benzene:



Diazonium Halides.—A study of the Friedel-Crafts reaction of benzenediazonium chloride with aromatic hydrocarbons and aluminum chloride was made by Möhlau and Berger,[335] who found that with benzene the following reactions occurred:

(1) $C_6H_5N_2Cl + C_6H_6 \longrightarrow HCl + C_6H_5.N_2.C_6H_5$

(2) $C_6H_5N_2Cl + C_6H_6 \longrightarrow HCl + N_2 + C_6H_5.C_6H_5$

(3) $C_6H_5.N_2.Cl \longrightarrow N_2 + C_6H_5.Cl$

In reaction (1) the chlorine atom of benzenediazonium chloride is simply replaced by the phenyl group. A cleavage of nitrogen also occurs, however, thus giving rise to biphenyl, as in reaction (2). Some of the benzenediazonium chloride undergoing cleavage remains as chlorobenzene, as shown in reaction (3). The two main reaction products are biphenyl and chlorobenzene.

The production of biphenyl here offers a method for the introduction of aromatic groups into the benzene nucleus by using benzenediazonium chloride. Instead of benzene, the reaction was shown to take place also with toluene, biphenyl, and naphthalene. With toluene, a mixture of *o*- and *p*-phenyltolyl was secured. The use of biphenyl gives *p*-xenyl benzene and an isomer. With naphthalene a mixture of α- and β-phenylnaphthalene is obtained. In all cases, chlorobenzene, from cleavage of the benzenediazonium chloride used, was obtained as by-product.

The reaction was also extended to the introduction of heterocyclic rings into the benzene nucleus, the following compounds being obtained from benzenediazonium chloride with anhydrous aluminum chloride and the indicated reactants:

Reactant	Products
thiophene	β-phenylthiophene
pyridine	α- and γ-phenylpyridines
quinoline	*l*-phenylquinoline

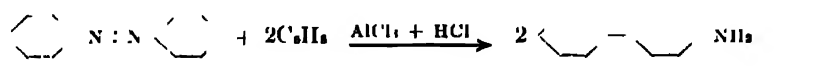
[334] U. S. P. 2,012,569 (1935) to G. Kranzlein, P. Ochwat, and K. Moldaenke (to General Aniline Works); *C. A.*, **29**, 8005.

[335] R. Möhlau and R. Berger, *Ber.*, **26**, 1994-2004, 1196-1200 (1893).

It has also been shown that β-naphthalenediazonium chloride reacts as does benzenediazonium chloride in the reaction.

The yields of substituted benzenes in all these cases are necessarily small, because of the simultaneous formation of the other products already mentioned. In using Möhlau and Berger's procedure for the preparation of methylbiphenyl from benzenediazonium chloride and toluene, a 30 per cent yield of the pure product, m. 264°, was secured by Knowles.[336]

An interesting reaction which may be mentioned here is the condensation of azobenzene with benzene and other aromatic hydrocarbons in the presence of aluminum chloride and hydrogen chloride. With benzene, *p*-aminobiphenyl is formed in a 70-80 per cent yield.



The reaction proceeds even more readily when the benzene is replaced by toluene or xylene.[337]

With toluene it is so vigorous that the temperature should not be allowed to rise above 10-15°. Here the product consists of a mixture of the hydrochlorides of 4'-amino-4-methylbiphenyl, benzidine, and aniline. Naphthalene and azobenzene undergo a similar reaction.[338]

An intermediate formation of azobenzene hydrochloride is assumed in the reaction. *o*-Azotoluene hydrochloride has been shown to react similarly, being transformed by benzene in the presence of aluminum chloride into the hydrochloride of 4-amino-3-methylbiphenyl.

Condensation of biphenyl with azobenzene in the presence of hydrogen chloride and aluminum chloride yields *p*-aminoterphenyl.[339] Biphenyl is dissolved in azobenzene, to which is added gaseous hydrogen chloride. Upon the separation of brown crystals of azobenzene chlorohydrate, aluminum chloride is added. The black reaction product is then decomposed with ice-hydrochloric acid and the unreacted biphenyl and azobenzene are separated. Thirty to 40 g of *p*-aminoterphenyl are secured from 100 g of biphenyl and 27 g of azobenzene.

The condensation of azobenzene with phenol in the presence of aluminum chloride has been likewise attempted, but it was found that zinc chloride was a better catalyst than aluminum chloride for the introduction of the *p*-aminophenyl residue into phenol. With aluminum chloride, dehydrogenation of the primarily formed hydrazo-compound was found to occur.[340]

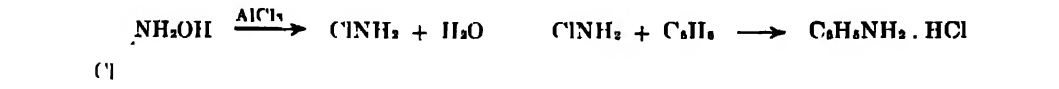
Halogen Salts of Amines.—Aniline salts may be condensed in the presence of aluminum chloride to diphenylamine. An intermediate formation of the complex, $(C_6H_5NH_2Cl)_3Al$, has been assumed. Aniline,

[336] C. L. K[illegible]es, *J. Am. Chem. Soc.*, 43, 896-898 (1921).
[337] R. Pumm[illegible]r and J. Binapfl, *Ber.*, 54, 2788-2784 (1921).
[338] R. Pummerer, J. Binapfl, K. Bittner, and K. Schuegraf, *Ber.*, 55, 3095-3104 (1922).
[339] R. Pummerer and K. Bittner, *Ber.*, 57, 84-88 (1924).
[340] R. Pummerer and M. Dally, *Ber.*, 59, 2175-2181 (1926).

alone, will also undergo the reaction, but the yields are lower. According to Gershzon and co-workers,[341] diphenylamine may be obtained in 75 per cent yield by heating a mixture consisting of 93 g of aniline, 93 g of aniline hydrochloride, and 30 g of aluminum chloride at the boiling point for 36 hours. It was subsequently stated that anhydrous aluminum chloride in this reaction cannot be replaced by the chlorides of iron, copper, or zinc.[342]

According to Gershzon and co-workers,[343] however, the reaction is catalyzed, apart from aluminum chloride, by a number of other substances (antimony trichloride, mercuric iodide, cuprous iodide, and cuprous chloride); but the yields of diphenylamine, and its purity, are lower.

It has been reported that by heating hydroxylamine hydrochloride with benzene or toluene in the presence of an excess of aluminum chloride, aniline or *p*-toluidine may be synthesized in low yields.[344] The condensation has been assumed by Böeseken [345] to proceed according to the scheme:



Halogenated Nitro- Compounds.—The Friedel-Crafts reaction has been little used with halogenated nitro- compounds. Negative results have been obtained with nitrosyl chloride and with chloropicrin. Nitro-compounds of the aliphatic series have received little attention until recently.[346] Their halogenated derivatives have pronounced halogenating and oxidizing tendencies,[347] and it is to be expected that normal Friedel-Crafts reaction would be hindered thereby. Since, in the aromatic series, nuclear halogen is replaced in the Friedel-Crafts reaction only in exceptional instances,* Friedel-Crafts condensation of nitro-halogeno-benzenes with replacement of halogen does not occur. Although, in the aralkyl series, nitrobenzyl chlorides undergo the reaction smoothly, higher nitrophenylalkyl halides fail to condense.

An attempt has been made to react nitrosyl chloride with aromatic hydrocarbons to yield nitroso- derivatives which could then be converted to nitro- compounds or amines.[348] It was hoped that the condensation would proceed:

[341] G. I. Gershzon and R. P. Lastovskii, *J. Applied Chem. (U.S.S.R.)*, 9, 502-504 (in German 504) (1936); *C. A.*, 30, 7550.
[342] M. Bezzubetz and E. Schapson, *Prom. Org. Chim.*, 4, 28-30 (1937); *Brit. Chem. Abs.*-B, 1938, 86. G. I. Gershzon, R. P. Lastovskii, and E. N. Shurygina, *Prom. Org. Chim.*, 4, 553-555 (1937); *C. A.*, 32, 7428.
[344] G. F. Jaubert, *Compt. rend.*, 132, 841-843 (1901); *J. Chem. Soc. Abs.*, 80 (I), 320 (1901). C. Graebe, *Ber.*, 34, 1778-1781 (1901).
[345] J. Böeseken, *Rec. trav. chim.*, 24, 6-18 (1905).
[346] H. B. Hass, E. B. Hodge, and B. M. Vanderbilt, *Ind. Eng. Chem.*, 28, 339-344 (1936).
[347] *cf.* H. N. Melnikow, *J. Gen. Chem. (U.S.S.R.)*, 7, 1546-1552 (1937); *C. Z.*, 1938, I, 572; *C. A.*, 31, 8504.
* *cf.* page 130.
[348] A. Schaarschmidt and M. Rasck, *Ber.*, 58, 348-352 (1925); *C. A.*, 19, 1567.

$$RH + NOCl \xrightarrow{AlCl_3} RNO + HCl$$

The reaction was prevented, however, by the formation of a very stable addition product of aluminum chloride and nitrosyl chloride, which at room temperature practically does not react at all with benzene. When the addition product was warmed with benzene, hydrogen chloride was evolved. Using 1 mole of nitrosyl chloride and 0.5 mole of aluminum chloride, the following products were obtained in the indicated amounts by heating for two hours at the following temperatures:

	60°	70°	80°
(I) *p*-Aminobiphenyl	...	. .	6 g
(II) Phenol, bases, and resinous products	6 g	24 g	58 g

Using 1 mole each of the reactants, and heating at the boiling point, 20 g of *p*-aminobiphenyl together with 60 g of the second product were obtained. When 1 mole of nitrosyl chloride was heated with aluminum chloride in 3 moles of benzene at 80° for ten hours, yields of both types of products increased greatly, 55 g of *p*-aminobiphenyl and 120 g of product (II) being obtained.

The course of the reaction may be explained by primary formation of a complex, $2AlCl_3.3C_6H_6.3NOCl$, which decomposes into hydrogen chloride, nitrosobenzene, and aluminum chloride. *p*-Aminobiphenyl is subsequently formed by reaction of the nitrosobenzene with benzene in the presence of aluminum chloride.

The condensation of chloropicrin, NO_2CCl_3, with benzene and aluminum chloride yields triphenyl carbinol, triphenylmethane, and diphenylmethane. The nitro- groups are mainly converted into nitrous acid, only a small amount of nitric oxide being formed. Chloropicrin reacts in the same way with phenol to yield aurin, $(C_6H_4OH)_2C{:}(C_6H_4O)$. With naphthalene it yields trinaphthyl carbinol, $(C_{10}H_7)_3COH$, as the main product of the reaction.[349] The chloropicrin is obviously decomposed during the reaction, so that the products are those which are obtained in Friedel-Crafts reactions with chloroform or carbon tetrachloride.

The reaction of bromonitromethane with benzene, bromo- and chlorobenzene, and anisole in the presence of aluminum chloride[350] leads to the formation of an aromatic nitromethane, or its decomposition products, and a bromine derivative of the aromatic component used in the reaction

With benzene, phenylnitromethane and its decomposition products, benzaldehyde and benzoic acid are formed by normal Friedel-Crafts condensation.

$$C_6H_6 + BrCH_2NO_2 \xrightarrow{AlCl_3} C_6H_5CH_2NO_2 + HBr$$

The ready decomposition of phenylnitromethane in the presence of acids may explain the formation of the aldehyde and carboxylic acid. Bromo-

[349] K. Elbs, *Ber.*, **16**, 1274-1277 (1883); *J. Chem. Soc. Abs.*, 100 (1883). C. Friedel and J. M. Crafts, *Ann. chim. et phys. (6)*, **1**, 449-532 (1884). E. Boedtker, *Bull. soc. chim. (4)*, **3**, 726-729 (1908); *C. A.*, **2**, 2892. K. Elbs and O Wittich, *Ber.*, **18**, 347-349 (1885); *J. Chem. Soc. Abs.*, **48**, 517 (1885)

[350] M. L. Sherrill, *J. Am. Chem. Soc.*, **46**, 2753-2758 (1924); *C. A.*, **19**, 48.

nitromethane also reacts as a brominating agent, so that bromobenzene is another product. In various runs the total percentages of Friedel-Crafts reaction products are 19-45 per cent. Bromobenzene is formed in yields of 12-30 per cent. The products formed in the two types of reaction account for from 40-80 per cent of the total bromonitromethane used.

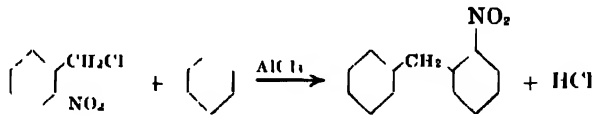
The reaction of bromobenzene and chlorobenzene with bromonitromethane proceeds in the same way. *p*-Substituents are obtained. With anisole, however, the condensation could not be effected as completely, most of the anisole being recovered unchanged. *p*-Bromoanisole was obtained, together with small amounts of anisaldehyde and anisic acid.

The tendency of bromonitromethane to act as both alkylating and halogenating agent may be explained on the assumption that it exists in two electromeric forms:

$$\overset{+}{\mathrm{Br}} \cdot \overset{-}{\mathrm{C}}\mathrm{H_2NO_2} \rightleftarrows \overset{-}{\mathrm{Br}} \cdot \overset{+}{\mathrm{C}}\mathrm{H_2NO_2}$$

In the first case the positive bromine atom acts as a brominating agent; in the second case, the negatively charged bromine acts as an alkyl halide.

o-Nitrobenzyl chloride condenses readily with benzene in the presence of anhydrous aluminum chloride to yield phenyl-(2-nitrophenyl)-methane [351]:



Upon gradual addition of 40 g of aluminum chloride into a mixture of 20 g of *o*-nitrobenzyl chloride, 80 cc of benzene and 100 cc of carbon disulfide, heating to the boiling point for two hours, and customary treatment of the reaction mixture, 18-22 g of the *o*-nitrodiphenylmethane is obtained.[352]

A resinous by-product, consisting of the hydrochlorides of two bases, is also obtained in the reaction.[353] One of the bases is a yellow compound, $C_{13}H_9ON$, m. 169°, and the other a colorless product, $C_{13}H_{11}N$, m. 83°. The yield of the first base is about 1.2 g from 20 g of *o*-nitrobenzyl chloride.[354]

Böeseken [355] has reported the formation of a complex of *p*-nitrobenzyl chloride with aluminum chloride, which reacts with benzene and its homologs at 50°, furnishing the corresponding *p*-nitrodiphenylmethanes. Since this additive product appears to be partially dissociated when dissolved in benzene, he suggests that it is the aluminum chloride so liberated which brings about the catalytic action. The formation of the

[351] R. Gergy and W. Koenigs, *Ber.*, 18, 2400-2407 (1885). W. Städel, G. Muth, and E. Meyer, *Ann.*, 283, 157-161 (1894). K. Schorlemmer, *J. prakt. Chem. (2)*, 65, 305-307 (1902).
[352] S. Gabriel and R. Stelzner, *Ber.*, 29, 1300-1316 (1896).
[353] M. Freund, *Monatsh.*, 17, 395-400 (1896); *J. Chem. Soc. Abs.*, 72 (I), 68 (1897).
[354] K. Drechsler, *Monatsh.*, 35, 533-560 (1914); *C. A.*, 8, 3033.
[355] J. Boeseken, *Rec. trav. chim.*, 23, 98-109 (1904); *J. Chem. Soc. Abs.*, 86 (I), 384 (1904).

complex may regulate the reaction only insofar as it prevents the destructive action of the condensing agent on the product formed. Although the yield of the final product is thus increased, the function of the complex would thus be that of hindering rather than accelerating the reaction. On the basis of condensations effected with *p*-nitrobenzyl chloride and benzene, toluene, or chlorobenzene, Böeseken assumes that complex formation occurs not by addition of the aluminum chloride at the chloromethylene, but probably at the nitro- group, and that the condensation may be expressed as

$$AlCl_3.p\text{-}NO_2.C_6H_4CH_2Cl + RH \longrightarrow AlCl_3.p\text{-}NO_2C_6H_4.CH_2.R + HCl$$

Such an assumption is made from the fact that whereas complexes in which the catalyst is bound in the vicinity of the halogen have an orienting effect on the resulting substitution, this directive influence is not exerted in condensations with *p*-nitrobenzyl chloride. Thus, although in the condensation of *p*-nitrobenzyl chloride with benzene, *p*-nitrodiphenylmethane alone is formed, with toluene an oily mixture of isomerides is obtained, and with chlorobenzene a mixture of *p*-chloro-*p'*-nitrodiphenylmethane and *o*-chloro-*p'*-nitrodiphenylmethane. Substitution in both the *ortho-* and *para-* positions is likewise obtained with bromobenzene.

Olivier and Berger[356] also assume that the catalytic effect of the reaction does not proceed through the chain. These investigators made a thermodynamic study of the condensation of nitrobenzyl chlorides with benzene, toluene, or chlorobenzene and aluminum chloride. In the reaction of *o-*, *m-*, and *p*-nitrobenzyl chloride with benzene in the presence of aluminum chloride, the velocity constants are > 0.025 for *o-*, 0.025 for *m-*, and 0.0046 for *p*-nitrobenzyl chloride (in excess benzene, $K_{AlCl_3} = 0.2$; $t = 30°$). Condensation of *p*-nitrobenzyl chloride, in the presence of 1 mole of the catalyst, proceeded most rapidly with toluene, more slowly with benzene, and most slowly with chlorobenzene. The constants were 0.0046 for benzene, 0.0105 for toluene, and 0.0008 for chlorobenzene (concentration of aluminum chloride and of nitrobenzyl chloride = .02; $t = 30°$). A correlation of these results with the principle of induced alternating polarity in organic compounds and the general and *ortho-* effect of substituents was perceived; and it appeared that the catalytic action of the aluminum chloride did not extend through the carbon chain, but that here the catalyst had a direct influence.

A disagreement with these views has been expressed by van Duin.[357] In his opinion, a strong alternating effect, transmitted through the carbon chain, is to be expected in the condensation, because of the red color which develops when the reacting components are brought together. Olivier's results appear to be not more or less negative indications of the principle of induced alternating polarity, but strongly positive proofs

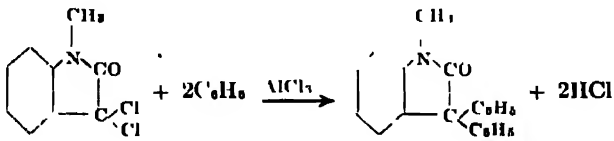
[356] S. C. J. Olivier and G. Berger, *Rec. trav. chim.*, **45**, 710-712 (1926); *C. Z.*, **1926**, II, 3038; *C. A.*, **21**, 2887.
[357] C. F. van Duin, *Rec. trav. chim.*, **46**, 256-257 (1927); *C. A.*, **21**, 3009.

According to Olivier and Berger,[358] however, the arguments in favor of strong alternating effect, based by van Duin on the development of the red color, are not valid because the reactivity of the non-colored system, $C_6H_5CH_2Cl.AlCl_3$, is greater than that of the colored system, $C_6H_4.(CH_2Cl)NO_2.AlCl_3$. Since the substituent NO_2AlCl_3 or $NO_2.AlCl_3$-C_6H_6 is more negative than the NO_2 group, and since the alternate effect in the case of the hydrolysis of the substituted benzyl chlorides decreases as the negativity of the substituent increases, it is to be expected that in the Friedel-Crafts reaction with nitrobenzyl chloride a decrease in alternate effect is indicated.

p-Nitrophenylethyl chloride, even after protracted treatment with benzene and aluminum chloride, yields oily products which still contain chlorine, and from which a chlorine-free nitro- compound cannot be isolated. *p*-Nitrophenylpropyl chloride behaves in a similar manner.[359]

Halogenated Ring Compounds of Nitrogen.—Only isolated instances of the application of the Friedel-Crafts reaction to the introduction of aryl groups into heterocyclic compounds of nitrogen have been reported.

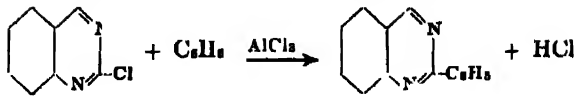
Although indirect methods have been generally used for the preparation of aryl-substituted ring compounds of nitrogen, Myers and Lindwall [360] state that the Friedel-Crafts reaction of N-methyl-3,3-dichlorooxindole with benzene and aluminum chloride proceeds smoothly. These investigators added slowly 0.0125 mole of aluminum chloride to 0.005 mole of the halogenated indole in 20 cc of absolute benzene and then heated the reaction mixture for four hours. After removing the solvent and decomposing the catalyst complex, a gummy mass resulted, which was extracted with dilute methyl alcohol. The extract was decolorized with charcoal. Upon cooling, the arylated indole, N-methyl-3,3-diphenyloxindole, separated as white needles from methyl alcohol, m.p. 171-171.5°. Normal Friedel-Crafts condensation had occurred:



N-ethyl-3,3-dichloroindole reacts similarly. Previously, Inagaki [361] had likewise prepared 3,3-diphenyloxindole from 3,3-dichlorooxindole and benzene in the presence of aluminum chloride.

The Friedel-Crafts reaction has also been used in the condensation of halogenated quinazoline and aromatic hydrocarbons or phenols with replacement of halogen. 2-Chloroquinazoline and benzene yield 2-phenylquinazoline.

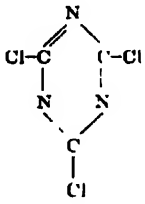
[358] C. J. Olivier and G. Berger, *Rec. trav. chim.*, **46**, 605-608 (1927); *C. A.*, **22**, 228.
[359] J. v. Braun, H. Deutsch, and O. Kosciolski, *Ber.*, **46**, 1511-1526 (1913).
[360] J. J. Myers and H. G. Lindwall, *J. Am. Chem. Soc.*, **60**, 2153-2155 (1938).
[361] S. Inagaki, *J. Pharm. Soc. Japan*, **53**, 686-678 (1933); *C. A.*, **28**, 2003.



Similar condensation of 4-chloroquinazoline and α-naphthol gives 4-(4'-hydroxy-α-naphthyl)-quinazoline, m.p. 230-232°. 2,4-Dichloroquinazoline reacts with replacement of both chlorines. The chloroquinazoline may also have a hydroxy- substituent; 2-chloro-4-hydroxy-quinazoline with benzene yields 4-hydroxy-2-phenylquinazoline, m.p. 235°. The presence of a nitro- substituent does not inhibit the reaction when a hydroxy-group is also present, for 2-chloro-6-nitro-4-hydroxy-quinazoline with naphthalene and aluminum chloride gives 6-nitro-4-hydroxy-2-α-naphthylquinazoline.[362]

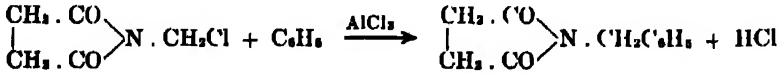
A chloro derivative of a pyrimidine compound has been shown to undergo normal Friedel-Crafts reaction wtih benzene and aluminum bromide, but 4-methyl-2,6-dichloropyridine failed to react with benzene and aluminum chloride.[302a]

The condensation of cyanuryl chloride,



with aromatic compounds in the presence of aluminum chloride is another example of halogen replacement in Friedel-Crafts reaction of halogenated ring compounds of nitrogen. Since cyanuryl chloride is a polymeric form of cyanogen chloride, its reactions have been cited together with those of cyanogen halides.*

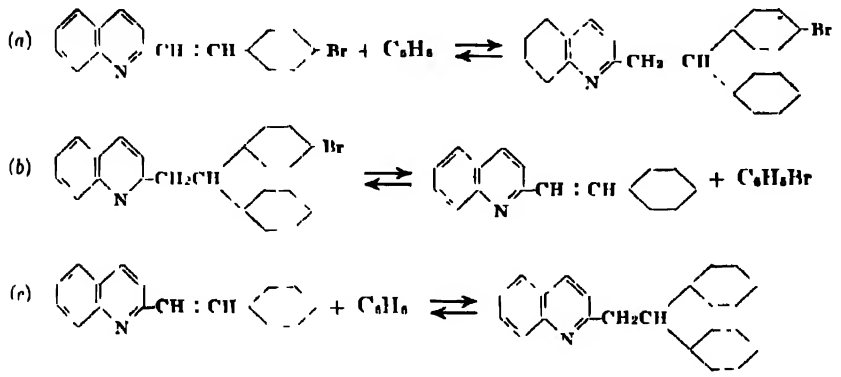
N-(Chloroalkyl)-cyclic imides may undergo Friedel-Crafts reaction Condensation of N-chloromethylsuccinimide with benzene in carbon disulfide in the presence of aluminum chloride proceeds with normal replacement of halogen to give N-benzylsuccinimide [363]:



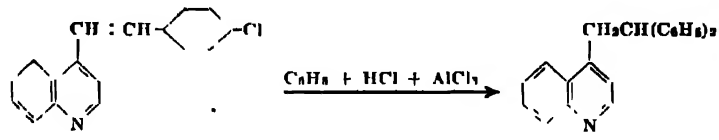
In an attempt to add benzene to *p*-chlorobenzalquinaldine in the presence of aluminum chloride it was found that condensation proceeded with removal of halogen to give a good yield of α-benzohydrylquinaldine.[304]

[362] Brit. P. 287,179 (1928) to I. G. Farbenindustrie. *Brit. Chem. Abstracts*-B, 747 (1929).
[362a] E. Ochiai, *J. Pharm. Soc. Japan*, 60, 164-74 (1940). *C. A.*, 34, 5449
* See page 148.
[363] E. Cherbuliez and G. Sulzer, *Helv. Chim. Acta*, 8, 567-571 (1925); *J. Chem. Soc. Abs.*, 128 (I), 1252 (1925).

An investigation of the mechanism of the reaction[365] showed that the removal of chlorine was not due to the action of aluminum chloride alone, for *p*-chlorobenzalquinaldine was unaffected by long contact with aluminum chloride. Reaction of *p*- or *m*-bromobenzalquinaldine with benzene and aluminum chloride also gave α-benzohydrylquinaldine. Since one of the reaction products with *p*-bromobenzalquinaldine was bromobenzene, it was assumed that condensation proceeds by replacement, not of the halogen atom, but of the entire halophenyl radical. The formation of α-benzohydrylquinaldine may be explained by reversible condensation according to the scheme:



In a further study of reversible condensations, *p*-chlorobenzallepidine was subjected to treatment with benzene in the presence of aluminum chloride.[366] α-Benzohydryllepidine was obtained.



The condensation is similar to the formation of α-benzohydrylquinaldine from *p*-chlorobenzalquinaldine and benzene under like conditions.

Halogenated Compounds of Sulfur

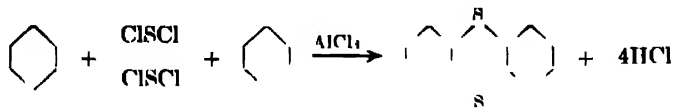
The preparation of diphenyl sulfide from benzene and sulfur dichloride in the presence of aluminum chloride resembles a Friedel-Crafts alkylation with dihalogenated paraffins; here sulfur is substituted for the alkyl residue in the typical equation:

$$2C_6H_6 + XRX \longrightarrow C_6H_5.R.C_6H_5 + 2HX$$
$$2C_6H_6 + ClSCl \longrightarrow C_6H_5.S.C_6H_5 + 2HCl$$

[365] R. C. Fuson, A. P. Kozacik, and J. T. Eaton, *J. Am. Chem. Soc.*, 55, 3799-3803 (1933).
[366] R. C. Fuson, L. J. Alexander, E. Ellingboe, and A. Hoffman, *J. Am. Chem. Soc.*, 58, 1970-1980 (1936). *C. A.*, 30, 8211.

When benzene is treated with sulfur dichloride in the presence of aluminum chloride at 0°, diphenyl sulfide is almost the sole product; but at 60° there are also produced chlorobenzene and thianthrene, the formation of these being due to the decomposition of the sulfur dichloride into the monochloride and chlorine, which then attack the benzene.[367]

The condensation of sulfur dichloride with benzene and aluminum chloride under certain conditions affords an excellent method for the preparation of thianthrene. Slow addition of a benzene solution of sulfur dichloride to a cooled solution of aluminum chloride, followed by gentle heating at 40-45°, has been reported[368] to give a good yield of thianthrene:



Another method consists in adding 100 g of aluminum chloride to 500 g of benzene, cooling to 0°, and then running in a solution of 200 g of sulfur dichloride in benzene. The reaction mixture is allowed to remain at ordinary temperature for five hours, and is subsequently boiled for two or three hours. Before isolation of the product, the reaction mixture is allowed to remain at ordinary temperature for fifteen hours. The yield of pure thianthrene is 136 g.[369]

Toluene with sulfur dichloride similarly yields ditolylene disulfide.[368]

Sulfur monochloride with benzene in the presence of aluminum chloride yields diphenyl sulfide,[367] according to the equation:

$$S_2Cl_2 + 2C_6H_6 + AlCl_3 \longrightarrow (C_6H_5)_2S\,AlCl + S + 2HCl$$

Diphenyl disulfide is always formed, either directly or by the action of sulfur on the diphenyl sulfide first formed. Other reactions taking place are those involving the formation of thianthrene, and of thiophenol[370]:

$$(C_6H_5)_2S_2 + S \longrightarrow H_2S + (C_6H_4S)_2$$
$$C_6H_6 + S \longrightarrow C_6H_5SH$$

Diphenyl sulfide has been prepared in 81-83 per cent yields by treating a mixture of 3.48 moles of aluminum chloride in 11 moles of dry benzene with a solution consisting of 3 moles of commercial sulfur chloride in 5 moles of benzene at about 10° during a period of one hour.[371]

Toluene with sulfur chloride and aluminum chloride yields 4,4'-dimethyldiphenyl sulfide, together with other products produced by secon-

[367] J. Boeseken, *Rec. trav. chim.*, 24, 209-222 (1905). *J. Chem. Soc. Abs.*, 88 (I), 583 (1905). *cf.* C. Friedel and J. M. Crafts, *Ann. chim. phys.* (6), 1, 350 (1884).
[368] F. Krafft and R. E. Lyons, *Ber.*, 29, 435-443 (1896). *J. Chem. Soc. Abs.*, 70, 297 (1896).
[369] K. Fries and W. Vogt, *Ann.*, 381, 312-336 (1911); *C. A.*, 5, 3442. *cf.* P. Genvresse, *Bull. soc. chim.* (3), 15, 409 (1896).
[370] J. Boeseken and D. A. W. Koning, *Rec. trav. chim.*, 30, 116-136 (1911); *C. A.*, 5, 3390.
[371] W. W. Hartman, L. A. Smith, and J. B. Dickey, *Org. Syntheses*, 14, 26-30 (1934); *cf. Ind. Eng. Chem.*, 24, 1317-1318 (1932); *C. A.*, 27, 71.

dary condensations of the primarily formed materials, as in the case of the like reaction with benzene.[370] Studies on the course of the reaction show that toluene and ditolyl sulfide are more easily attacked by sulfur than is benzene.

The action of sulfur chloride on chlorobenzene in the presence of aluminum chloride gives 4,4'-dichlorodiphenyl sulfide as the main product.[370] In this reaction, the chlorobenzene is not at all attacked by the sulfur freed during the condensation.

Products obtained by the condensation of sulfur chloride with aromatic hydrocarbons, for example benzene, toluene, and xylene, or their halogenated derivatives, in the presence of aluminum chloride, have been claimed for use in the preparation of flotation agents.[372]

An attempt was made to prepare nitrothianthrene by reaction of nitrobenzene with sulfur chloride and aluminum chloride, but the condensation did not take the expected course. Only a black, carbonaceous material was obtained from which no characteristic compounds could be isolated.[373]

Friedel-Crafts reaction of sulfur chloride with a dibenzanthrone or isodibenzanthrone at 100° in the presence of aluminum chloride may be used for the preparation of blue vat dyes.[374]

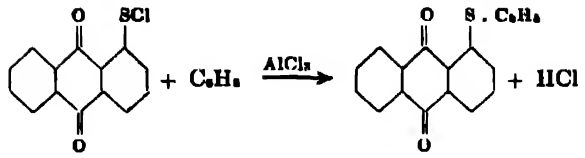
Substituted sulfur chlorides may undergo the Friedel-Crafts reaction with simple displacement of halogen. Thus thiophosgene with benzene and aluminum chloride yields thiobenzophenone [375]:

$$2C_6H_6 + CSCl_2 \xrightarrow{AlCl_3} (C_6H_5)_2CS + 2HCl$$

Benzene and trichloromethylsulfur chloride, $Cl_3C.SCl$, in the presence of aluminum chloride, yield thiobenzophenone, $C_6H_5.CS.C_6H_5$. Triphenylmethylsulfur chloride, $(C_6H_5)_3C.SCl$, similarly gives thiobenzophenone, but in lower yield.[376] The reaction obviously proceeds through the intermediate formation of thiophosgene. In the condensation of triphenylmethylsulfur chloride, the main reaction products are triphenylmethyl carbinol and hydrogen sulfide.[377] Of interest in this connection is the report that trichloromethylsulfonyl chloride, Cl_3CSO_2Cl, likewise yields triphenyl carbinol when treated with benzene and aluminum chloride.[378]

Reaction of 1-anthraquinonyl sulfur chloride with benzene and aluminum chloride proceeds smoothly, yielding 1-anthraquinonyl phenyl sulfide [379]:

[372] U. S. P. 1,875,062 (1932) to H. A. Lubs, A. L. Fox, and C. C. Smith (to E. I. du Pont).
[373] K. Ross, Dissertation. Marburg, 1913.
[374] Brit. P. 342,466 (1929) to I. G. Farbenindustrie; *Brit. Chem. Abstracts*-B, 476 (1931).
[375] H. Bergreen, *Ber.*, 21, 337-352 (1888).
[376] D. Vorländer and E. Mittag, *Ber.*, 52, 413-423 (1919).
[377] E. Mittag, Dissertation. Halle (Saale) (1915).
[378] M. Battegay and W. Kern, *Bull. soc. chim. (4)*, 41, 34-47 (1927); *C. A.*, 21, 1626.
[379] K. Fries and G. Schürmann, *Ber.*, 52, 2170-2181 (1919); *J. Chem. Soc. Abs.*, 118 (I), 166 (1920).

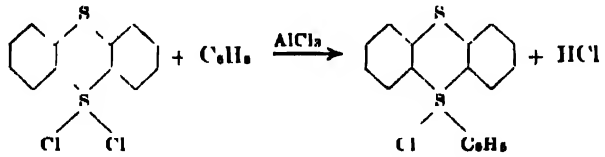


Condensation of 2-anthraquinonyl sulfur chloride with aromatic hydrocarbons proceeds similarly, with formation of 2-anthraquinonyl aryl sulfides.[380]

The condensation has been successfully applied to the preparation of tri-aryl sulfonium salts and to those containing cyclic aryl sulfides.[381] Reaction of bis-(*p*-bromophenyl)sulfonium dichloride and benzene proceeds with formation of phenyl-bis-(*p*-bromophenyl)sulfonium chloride in a 36.6 per cent yield (based on the dibromodiphenyl sulfide used previous to conversion to dichloride). The condensation proceeded according to the scheme:

$$(p\text{-BrC}_6\text{H}_4)_2\text{SCl}_2 + \text{C}_6\text{H}_6 \xrightarrow{\text{AlCl}_3} (p\text{-BrC}_6\text{H}_4)_2\text{S}(\text{Cl})\text{C}_6\text{H}_5 + \text{HCl}$$

Reaction of 5,5-dichlorothianthrene with benzene took a similar course, with replacement of one halogen to give 5-phenyl-5-chlorothianthrene:



5-Phenetyl-5-chlorothianthrene is obtained when phenetole is substituted for benzene in the foregoing reaction.

Friedel-Crafts condensation, with replacement of halogen, does not occur with halogeno-alkyl esters of sulfonic acid and aromatic hydrocarbons in the presence of aluminum chloride. Instead, cleavage of the sulfonate results, with subsequent condensation of aromatic hydrocarbon with the alkyl residue. Thus β-chloroethyltoluene-*p*-sulfonate gives a good yield of bibenzyl when treated with benzene and aluminum chloride[382]:

$$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OCH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{C}_6\text{H}_6 + \text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_2 . \text{CH}_2 . \text{C}_6\text{H}_5$$

Alkyl esters of chlorosulfonic acid cannot be used for the preparation of alkylbenzenesulfonates by the Friedel-Crafts reaction. Butyl chlorosulfonate and *n*-butyl chlorosulfite with benzene and aluminum chloride yield mainly butyl benzenes.[383]

[380] K. Fries, *Ber.*, 45, 2965-2973 (1912).
[381] G. Dougherty and P. D. Hammond, *J. Am. Chem. Soc.*, 61, 80-81 (1939).
[382] C. R. Clemo and E. Walton, *J. Chem. Soc.*, 723-729 (1928).
[383] C. Barkenbus, R. L. Hopkins, and J. F. Allen, *J. Am. Chem. Soc.*, 61, 2452-2453 (1939).

Halogenated Compounds of Selenium

The interaction of selenium tetrachloride with benzene in the presence of aluminum chloride has been the subject of several polemical papers. Contradictory results were obtained by early investigators.[384] Later workers[385] showed that the products of the reaction from 50 g of selenium tetrachloride were:

(a) chlorobenzene (1 g)
(b) diphenyl selenide (20 g)
(c) diphenyl diselenide (5 g)
(d) triphenyl selenonium chloride

The following equations were proposed to explain the formation of these products:

$$SeCl_4 + 3C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_2SeCl + 3HCl$$

$$(C_6H_5)_2SeCl \xrightarrow{heat} (C_6H_5)_2Se + C_6H_5Cl$$

$$(C_6H_5)_2Se + Se \xrightarrow{heat} (C_6H_5)_2Se_2$$

The triphenyl selenonium chloride was isolated as its zinc chloride addition compound (20 g).

Because the reaction of selenium tetrachloride with benzene and aluminum chloride forms so many compounds, it has been thought best, for the preparation of aromatic selenonium salts, to use a compound in which some of the halogen atoms of selenium tetrachloride were already replaced by organic groups. Condensation of diphenyl selenium dichloride with benzene and aluminum chloride was accordingly effected, giving a 66-67 per cent yield of triphenyl selenonium chloride[386]:

$$(C_6H_5)_2SeCl_2 + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3SeCl + HCl$$

Diphenyl-*p*-tolylselenonium chloride results similarly from diphenyl selenium dichloride and toluene with aluminum chloride. Under like conditions, bis-(*p*-tolyl)selenium dichloride and toluene yields tris-*p*-tolylselenonium chloride.[387]

Reactions involving acylation * with selenium compounds are discussed elsewhere in this book.

Halogenated Compounds of Phosphorus

The reaction of phosphorus trichloride with many aromatic compounds

[384] C. Chabrie, *Bull. soc. chim.* *(2)*, 50, 133-137 (1888); *(3)*, 2, 796 (1889); *(3)*, 11, 1080-1083 (1894); *Compt. rend.*, 109, 182-185 (1889); *J. Chem. Soc. Abs.*, 56, 41 (1889). F. Krafft and W. Worster, *Ber.*, 26, 2813-2822 (1893). F. Krafft and R. E. Lyons, *Ber.*, 27, 1761-1768 (1894). F. Krafft and A. Kasehau, *Ber.*, 29, 429-435 (1896).

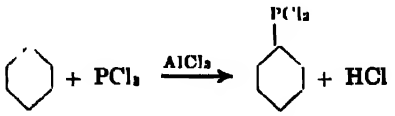
[385] W. E. Bradt and J. F. Green, *Proc. Ind. Acad. Sci.*, 41, 227-233 (1931). W. E. Bradt and H. Crowell, *Ibid.*, 41, 215-225 (1931). W. E. Bradt and J. F. Green, *J. Org. Chem.*, 1, 540-43 (1937).

[386] H. M. Leicester, *Org. Syntheses*, 18, 30-32 (1938); H. M. Leicester and F. W. Bergstrom, *J. Am. Chem. Soc.*, 51, 3587-3591 (1929).

[387] H. M. Leicester and F. W. Bergstrom, *J. Am. Chem. Soc.*, 54, 4428-4436 (1931); *C. A.*, 26, 439.

* See pages 269 and 393.

in the presence of aluminum chloride has been studied by Michaelis.[388] Chlorophosphines of the aromatic series are obtained:



The reaction proceeds very slowly with benzene, but much more readily with substituted benzenes, giving very good yields in some cases. Chlorophosphines of toluene, the xylenes, ethylbenzene, and pseudocumene are easily obtained by this method. The reaction proceeds somewhat more difficultly with mesitylene, cumene, cymene, bibenzyl, biphenyl, and diphenylmethane. Good results are obtained with tertiary amines, anisole, phenetole, and chloro- or bromobenzene. However, the chlorophosphine residue could not be introduced into iodobenzene, benzonitrile, benzophenone, and ethyl benzoate; it was introduced, but with great difficulty, into chloro- and bromo-toluene.

The following procedure was generally used: 150 g of the hydrocarbon was mixed with 200 g of phosphorus trichloride and 30 g of aluminum chloride. The whole mass was heated for 30 hours under reflux, at first gently and then vigorously. The addition of aluminum chloride, together with heating, results in a weak but gradual evolution of hydrogen chloride which is completely driven off at the conclusion of the reflux period The material separates into two layers, the lower being thick and brown colored while the upper is very fluid and almost colorless.

The mass is shaken repeatedly with dry petroleum ether boiling under 100° until the residue becomes an almost solid brown mass, from which the petroleum ether solution readily separates. In this solution are found the chlorophosphine and a considerable amount of aluminum chloride; unless the latter is removed, decomposition of the greater part of the product will occur during the subsequent distillation. To this end the ether solution is allowed to stand twelve hours in a loosely corked flask, during which time some brown viscous liquid separates. This contains all the aluminum chloride. The purified solution is then distilled on a water-bath to remove the solvent and any phosphorus trichloride; then it is heated to 140-150°. As a precaution the flask is allowed to cool, and a small portion is diluted with dry petroleum ether. Clouding of the solution indicates that all the aluminum chloride has not been removed. Accordingly, the whole mass must be retreated with petroleum ether as before and redistilled. The residue obtained at 150° is fractionated in a stream of carbon dioxide.

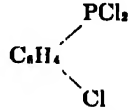
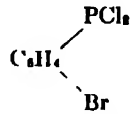
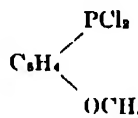
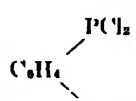
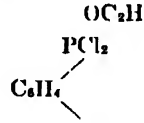
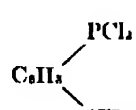
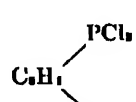
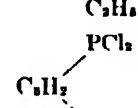
The yield of chlorophosphine is, of course, dependent on the nature of the hydrocarbon involved and the procedure must be modified when the boiling range of the chlorophosphine produced demands it. With toluene, *m*- or *p*-xylene, and ethylbenzene, the yield amounts to 25-30 per cent

[388] A. Michaelis, *Ann.*, 293, 193-325 (1896); *Ann.*, 294, 1-55 (1896); *Ann.*, 315, 43-103 (1901); *Ber* 12, 1009 (1879); A. Michaelis and C. Panek, *Ber.*, 13, 653-656 (1880); *Ann.*, 212, 203-220 (1882).

Mesitylene, however, only gives 3 to 5 per cent based on hydrocarbon used. This is believed to be due to the poor quality of the aluminum chloride.

In the production of anisyl- and phenetylchlorophosphines it is necessary to use aluminum chloride containing the oxychloride, since pure aluminum chloride causes cleavage of the alkoxy- groups, with resultant formation of phenyl-*o*-chlorophosphine.

The following chlorophosphines were prepared:

Chlorophosphine		b.p. (°C.)
Phenyl	$C_6H_5PCl_2$	224
p-Monochlorophenyl		254
p-Monobromopheny		272
p-Anisyl		250
p-Phenetyl		266
Tolyl		
para-		245
meta-		235
ortho-		244
Xylyl		
3,4-		257
2,4		254
p-Ethylbenzene		251
Pseudocumyl [2,4,5]		279

Chlorophosphine		b.p. (°C.)
Mesityl	$C_6H_3(PCl_2)(CH_3)_3$	274
Cumyl	$C_6H_4(PCl_2)C_3H_7$	269
Cymyl	$C_6H_3(PCl_2)(CH_3)C_3H_7$	276
Diphenylmethane	$C_6H_4(PCl_2)CH_2.C_6H_5$	221 (20 mm)
Bibenzyl	$C_6H_4(PCl_2)CH_2.CH_2C_6H_5$	250 (60 mm)

The purity of the product which Michaelis obtained from anisole has been questioned by Kamaĭ[389] who has suggested that the *p*-methoxydiphenylchlorophosphine of Michaelis was really contaminated with anisole, the boiling point of the pure product being found by Kamaĭ to be 140-140.5°/11 mm.

The reaction has also been applied to diphenyl ether, for the formation of *p*-phenoxyphenyldichlorophosphine[390]:

Tetrahydronaphthalene or decahydronaphthalene have been claimed to undergo like condensation.[391]

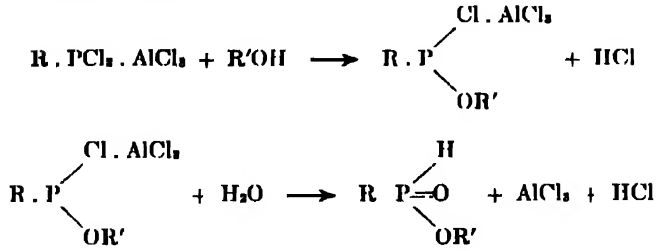
Lindner and his co-workers have prepared a number of aromatic halogen phosphines and have investigated their suitability for volumetric determination of water. A slightly modified Michaelis method was used for the preparation of tolyl-, naphthyl-, and xenyldichlorophosphines.[391a]

A comprehensive patent[392] covers reaction of phosphorus trichloride with hydrocarbons in general, subsequent hydrolysis, and if desired, reaction with alcohol for the production of esters of phosphinic acids. Phosphinic acids are formed according to the scheme:

[389] G. Kamaĭ, *J. Gen. Chem. U.S.S.R.*, 4, 192-193 (1934); *C. A.*, 29, 464.
[390] W. C. Davies and C. J. O. R. Morris, *J. Chem. Soc.*, 2880-2883 (1932); *C. A.*, 27, 966.
[391] German P. 452,064 (1927) to Leopold Cassella and Co.; *C. A.*, 22, 4129.
[391a] J. Lindner, *Ber.*, 55, 2025 (1922); *Z. analyt. Chem.*, 66, 305 (1925), 86, 141 (1931); *Monatsh.*, 53, 263, 274 (1929), 70, 1-19 (1937).
[392] U. S. P. 2,137,792 (1938) to W. H. Woodstock (to Victor Chemical Works).

$$RH + PCl_3 + AlCl_3 \longrightarrow R.PCl_2.AlCl_3 + HCl$$
$$R.PCl_2.AlCl_3 + 2H_2O \longrightarrow R.PHO(OH) + AlCl_3 + 2HCl$$

Formation of esters may proceed:



Condensations of phosphorus trichloride with aliphatic hydrocarbons is discussed in that section of this book dealing with Friedel-Crafts reactions in the aliphatic series.* A review of reactions with phosphoryl chloride has been included in the section of this book dealing with acid chlorides.†

Halogenated Compounds of Arsenic

Arsenic may be added to the benzene nucleus by the addition of aluminum chloride to a boiling solution of arsenic chloride in an excess of benzene [393]:

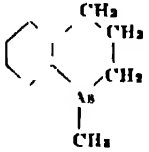
$$3C_6H_6 + AsCl_3 \longrightarrow (C_6H_5)_3As + 3HCl$$
$$2C_6H_6 + AsCl_3 \longrightarrow (C_6H_5)_2AsCl + 2HCl$$
$$C_6H_6 + AsCl \longrightarrow C_6H_5AsCl_2 + HCl$$

Triphenylarsine is the main product, with smaller amounts of phenyl arsine dichloride and diphenylarsine chloride. Since aromatic arsenic derivatives are decomposed by aluminum chloride, 30-40 per cent of the total arsenic present is recovered as the free element. Attempts to react styrene with arsenic chloride and aluminum chloride gave polymers of unknown composition.[394]

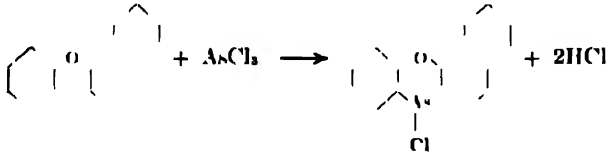
The preparation of tertiary arsines has also been studied by Hunt and Turner,[395] who observed that phenylmethylchloroarsine, $C_6H_5As(CH_3)Cl$, reacted with toluene, mesitylene, or bromobenzene in the presence of aluminum chloride to form phenyl-*p*-tolylmethylarsine, phenylmesitylmethylarsine, or phenyl-*p*-bromophenylmethylarsine, respectively, as reaction products. In an analogous manner benzene reacts to form diphenylmethylarsine [396]; but when an attempt was made to react benzene with (γ-phenyl-*n*-propyl)methylchloroarsine in the presence of aluminum chloride, no phenylpropylphenylmethylarsine was obtained;

* See Chapter 17.
† See page 269.
[393] H. Wieland and A. Kulenkampff, *Ann.*, 431, 30-33 (1923); W. La Coste and A. Michaelis, *Ann.*, 201, 184-201 (1880).
[394] A. F. Hunt and E. E. Turner, *J. Chem. Soc.*, 127, 906-909 (1925)
[395] A. F. Hunt and E. E. Turner, *J. Chem. Soc.*, 127, 2667-2671 (1925)
[396] G. J. Burrows and E. E. Turner, *J. Chem. Soc.*, 119, 426 (1921)

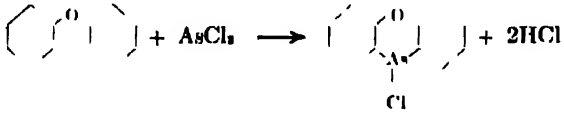
instead, ring closure took place, with the formation of *As*-methyltetrahydroarsinoline:



Phenyl α-naphthyl ether condenses with arsenic chloride and aluminum chloride, giving 7-chloro- α, β-naphthaphenoxarsine [397]:



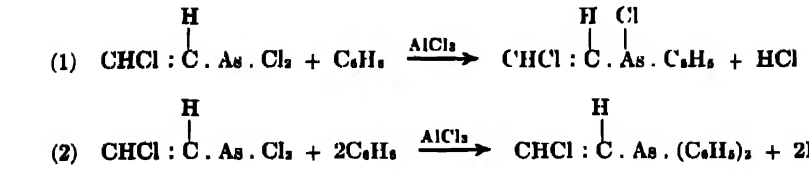
A like condensation occurs with diphenyl ether, yielding 6-chlorophenoxarsine [398]:



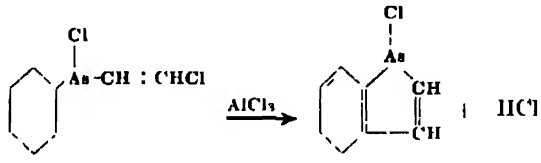
Phenyldichloroarsine absorbs acetylene in the presence of aluminum chloride to form β-chlorovinylphenylchloroarsine,β,β′-dichlorodivinylphenylarsine, and β-chlorovinyldiphenylarsine.[399] A crystalline complex, $AsPhCl_2.AlCl_3$, is formed initially, and if the reaction is not kept cool decomposition to β-chlorovinylarsine and benzene occurs.

The reaction of the chlorovinylarsines with benzene in the presence of aluminum chloride has produced conflicting results. Gibson and Johnson [400] reacted β-chlorovinyldichloroarsine, or β,β′-dichlorodivinylchloroarsine, or β,β′,β″-trichlorotrivinylarsine with benzene and aluminum chloride and in all cases obtained 9,10-dimethylanthracene as the main product. Such a reaction is analogous to that obtained with vinyl chloride on benzene in the presence of aluminum chloride.[401] Although higher-boiling products were obtained in this reaction, there was no indication of any heterocyclic arsenic compounds. Later, however, Das-Gupta [402] prepared phenyl-β-chlorovinylchloroarsine and diphenyl-β-chlorovinylarsine by heating chlorovinyldichloroarsine with benzene and aluminum chloride Condensation occurred with replacement of one or both arsenic-halogens:

[397] J. A. Aeschlimann, *J. Chem. Soc.*, 127, 811-815 (1925)
[398] W. Lewis, C. D. Lowry, and F. H. Bergeim, *J. Am Chem. Soc*, 43, 891-896 (1921)
[399] A. F. Hunt and E. E. Turner, *J. Chem. Soc.*, 127, 996-999 (1925); H. N. Das-Gupta, *J. Indian Chem. Soc.*, 14, 349-353 (1937); *C. A.*, 31, 8532.
[400] C. S. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, 2785-2786 (1930); *J. Chem. Soc.*, 753-756 (1931)
[401] *cf.* J. W. Cook, *Chem. and Ind.*, 50, 28 (1931).
[402] H. N. Das-Gupta, *J. Indian Chem. Soc.*, 14, 231-236 (1937); *Brit. Chem. Abstracts*-A (II), 435 (1937).



Treatment of phenyl-β-chlorovinylchloroarsine with aluminum chloride resulted in ring closure, with production of 1-chloroarsindole:



Halogenated Compounds of Silicon

In an attempt to apply the Friedel-Crafts reaction to the production of alkyl derivatives of aromatic silicon compounds, a condensation was tried with diphenylsilicon dichloride and ethyl bromide in the presence of aluminum chloride.[103] The catalyst was found to dissolve in diphenylsilicon dichloride without evolution of hydrogen chloride. Upon addition of ethyl bromide, reaction occurred, with formation of phenylsilicon trichloride, silicon tetrachloride and ethylbenzene and evolution of hydrogen chloride. Scission at the silicon bond had resulted, probably according to the scheme:

$$\left.\begin{array}{l} Si(C_6H_5)_2Cl_2 + AlCl_3 - \\ SiC_6H_5Cl_3 + AlCl_3 \end{array}\right\rangle \begin{array}{l} C_6H_5AlCl_2 + SiC_6H_5Cl_3 \\ C_6H_5AlCl_2 + SiCl_4 \end{array}$$

Ethylbenzene was formed by reaction of the benzene-aluminum chloride complex with the alkyl halide present.

Other phenyl derivatives of silicon were found to be decomposed by aluminum chloride, probably in an analogous manner.

Alkylation of Compounds Other Than Aromatic Hydrocarbons

The effect of alkyl substituents in the benzene ring on the course of Friedel-Crafts alkylation with halogenated hydrocarbons has already been discussed.* It is to be expected that other substituents also influence orientation and reaction velocity in condensations of this type. Halogenated aromatic hydrocarbons, phenols, and phenol ethers undergo Friedel-Crafts alkylation. Isolated instances of the alkylation of aromatic or aralkyl ketones, esters, and aldehydes have been reported. The reaction has likewise been applied to compounds of nitrogen and of sulfur.

[103] W. C. Evison and F. S. Kipping, *J. Chem. Soc.*, 2774-2778 (1931)

* See page 80.

In surveying condensations of this type, it is at once obvious that Friedel-Crafts alkylation of compounds other than aromatic hydrocarbons has not been so widely applied as acylation.† In the condensations with acyl halides, phenols and phenol ethers react even more readily than do hydrocarbons. In Friedel-Crafts alkylations, however, the presence of a hydroxy- or an alkoxy- group does not seem to have such an activating effect. The fact that in alkylations of phenols or ethers molar quantities of catalyst are often required,[404] whereas reaction with the corresponding hydrocarbon requires only catalytic amounts, coupled with the fact that in other instances severe conditions have been found necessary to bring about condensations which occur readily with aromatic hydrocarbons,[405] also indicates that substitution of so-called "activating groups" in the benzene ring does not necessarily imply greater reactivity in Friedel-Crafts alkylations.

A discussion is here given of aluminum chloride-catalyzed condensations, with halogen replacement, of halogenated compounds other than acyl halides and

halogenated aromatic hydrocarbons,
phenols,
phenol ethers,
ketones,
esters,
aldehydes,
compounds of nitrogen,
compounds of sulfur,
ring compounds of oxygen.

Halogenated Aromatic Hydrocarbons

The presence of halogen in the nucleus has a somewhat inhibiting effect on Friedel-Crafts alkylation. This may be partly due to the fact that aluminum chloride exerts a migrating effect on the halogen, so that reaction may be complicated by halogen cleavage and alkylation of the dehalogenated aromatic. The formation of alkylated halogeno-benzenes may, therefore, depend upon the speed with which condensation is effected. Highly active alkyl halides may react with the halogenobenzene before the catalyst has had time to exert its disruptive action.

According to Friedel and Crafts,[406] alkylation of halogenated benzenes with methyl chloride leads to very complicated results. *o*-Dichlorobenzene with 20 per cent of aluminum chloride was heated on a water-bath, and treated with a current of dry methyl chloride for about ten hours. The fact that the chief products were hexamethylbenzene and trichloromesitylene indicates migration of chlorine atoms. Friedel and Crafts

† See Chapter 6.

[404] U. S. P. 2,064,885 (1936) to M. S. Carpenter (to Givaudan-Delawanna, Inc.).

[405] *Cf.* U. S. P. 2,091,483 (1937) to J. F. Olin (to Sharples Solvents Corp.) for reaction of butyl halides with phenol; and T. Fuls, *Recueils Chem.*, 14, 87-92 (1934); *C. A.*, **28**, 6426, for like reaction with benzene.

[406] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 10, 411-424 (1887); *J. Chem. Soc. Abs.*, 52, 1101 (1887).

postulated the intermediate formation of an organometallic compound from dichlorobenzene, with displacement of chlorine and not of hydrogen. Such a compound, $C_6H_4.Al_2Cl_6$, in uniting with the alkyl halide, would result in the formation of a hexa-alkylated benzene. The formation of trichloro-mesitylene was thought to have been due to the migration of the displaced chlorine. The action of methyl chloride on dibromo-*o*-xylene in the presence of aluminum chloride gave a mixture of substances from which no definite products could be obtained.

The migrating action of aluminum chloride on halogen-containing compounds is well known, and is taken up in greater detail in another section of this book.* In alkylation, this tendency seems to be lessened as the number of carbon atoms in the alkyl halide increases.

Recently the condensation of isopropyl chloride with bromobenzene has been shown to take a more normal course. Upon adding, under cooling, 9.6 moles of isopropyl chloride to a mixture of 14.2 moles of bromobenzene and 0.9 mole of powdered aluminum chloride, allowing the reaction mixture to stand at 0° for thirty minutes, and then heating it on a steam-bath for fifteen minutes, a good yield of 4-bromoisopropylbenzene has been obtained. 1,3-Diisopropyl-4-bromobenzene was secured as a by-product in the reaction.[407] The course of the reaction is influenced by the type of halogen substituent and the presence of other substituents in the aromatic component, as well as by the reactivity of the alkyl halide used.

By condensing chlorobenzene with *tert*-butyl chloride, isobutyl chloride, or *n*-butyl chloride in the presence of aluminum chloride, *p*-chloro-*tert*-butylbenzene (b.p. 211°/759 mm) has been obtained. When bromobenzene is similarly treated, however, the principal product is a fraction boiling at 225-226°, and only a small quantity of the expected *p*-bromo-*tert*-butylbenzene (b.p. 232-233°) is obtained. Here bromine in the nucleus obviously interferes with a straight alkylation.[408]

A method for the manufacture of *meta*-alkyl phenols is based on the reaction of chlorobenzene with an alkyl halide and aluminum chloride to produce a mixture consisting largely of the *meta*-alkylhalobenzene and minor amounts of *ortho*- and *para*- isomers, and subsequently hydrolyzing the mixture to produce the corresponding alkyl phenols.[409]

In the condensation of *m*-bromotoluene with isobutyl chloride and aluminum chloride, the chief product is 5-bromo-1-methyl-3-*tert*-butylbenzene.[410] *p*-Iodo-*tert*-butylbenzene, together with *p*-di-iodobenzene, is obtained when iodobenzene is treated with isobutyl chloride and aluminum chloride and metallic aluminum.[408]

Isoamyl chloride condensed with chlorobenzene in the presence of alu-

* See Chapter 15.

[407] W. F. Bruce and F. Todd, *J. Am. Chem. Soc.*, **61**, 157-161 (1939); *C. A.*, **33**, 1723; *cf.* E. Boedtker *Bull. soc. chim. (5)*, **35**, 829 (1906).

[408] E. Boedtker, *Bull. soc. chim. (5)*, **35**, 825-836 (1906); *J. Chem. Soc. Abs.*, **90** (I), 942 (1906).

[409] U. S. P. 2,193,760 (1940) to R. R. Dreisbach, E. C. Britton, and R. P. Perkins (to the Dow Chemical Co.).

[410] German P. 86,477 to Fabr. de Thann et Mulhouse.

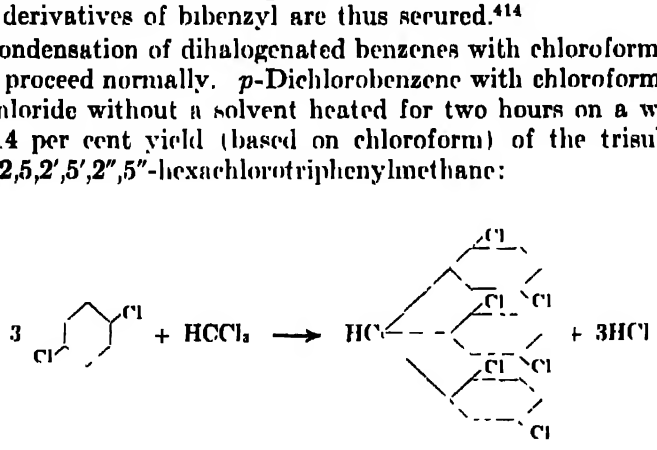
minum chloride yields *p*-chloro-*tert*-amylbenzene (b.p. 229°). *p*-Bromo-*tert*-amylbenzene (b.p. 246°) is similarly prepared.[411]

Friedel-Crafts condensation of chlorinated or brominated biphenyls with alkyl halides of less than 6 carbon atoms has been claimed to give the corresponding alkyl derivatives of the halogenated biphenyls.[412]

The condensation of dihalogenated aliphatic hydrocarbons with halogenated aromatic hydrocarbons in the presence of aluminum chloride leads to the production of plastic materials. The reaction of polyhalogenated hydrocarbons, such as ethylene dichloride, propylene dichloride, ethylene dibromide, or chlorinated paraffin wax with an aromatic hydrocarbon containing nuclearly substituted halogen in the presence of aluminum chloride results in condensation products which may be used in the production of non-inflammable compositions from chlorinated rubber.[413]

Products suitable for use in electric insulation may be obtained by treating with aluminum chloride a mixture of ethylene dichloride and a halogenated benzene, containing at least one replaceable hydrogen atom Chlorine derivatives of bibenzyl are thus secured.[414]

The condensation of dihalogenated benzenes with chloroform has been shown to proceed normally. *p*-Dichlorobenzene with chloroform and aluminum chloride without a solvent heated for two hours on a water-bath gives a 14 per cent yield (based on chloroform) of the trisubstitution product, 2,5,2′,5′,2″,5″-hexachlorotriphenylmethane:

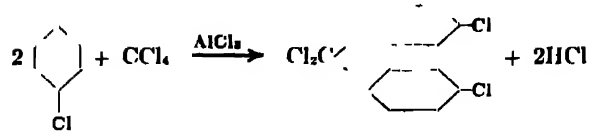


A 52 per cent yield (based on chloroform) of the corresponding bromo-derivative by reaction of *p*-dibromobenzene with chloroform and aluminum chloride was secured. Condensation was effected by allowing the reaction mixture to stand for several days at room temperature, with gentle shaking.[415]

Although triphenylmethane may be obtained by Friedel-Crafts reaction of carbon tetrachloride with benzene, like reactions with halogenated benzenes do not give triphenylmethane derivatives. Carbon tetrachloride with chlorobenzene and aluminum chloride in carbon disulfide gives 4,4′-dichlorobenzophenone chloride, together with some 2,4′-dichlorobenzo-

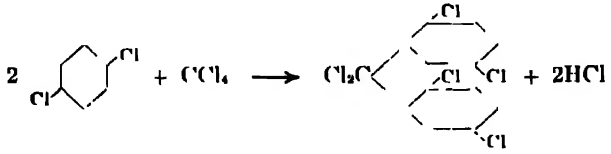
[411] E. Gleditsch, *Bull. soc. chim. (3)*, 35, 1094-1097 (1906); *J. Chem. Soc. Abs.*, 92 (I), 14 (1907).
[412] U. S. P. 2,172,391 (1939) to H. J. Kraus (to Monsanto Chemical Company).
[413] U. S. P. 2,136,270 (1938) to N. Bennett (to Imperial Chemical Industries).
[414] U. S. P. 2,083,612 (1936) to F. M. Clark and W. M. Kuts (to General Electric Co.); *C. A.*, 30, 2991.
[415] S. D. Wilson and Hsiao-Yun Huang, *J. Chinese Chem. Soc.*, 4, 1428 (1936); *C. Z.*, 1936, II 3788; see also S. D. Wilson and Y. Cheng, *J. Org. Chem.*, 5, 228-236 (1940) for analogous reactions with *o*- and *m*-dichlorobenzenes.

phenone. Only two chlorine atoms of the carbon tetrachloride are substituted:



Bromobenzene reacts similarly.[416]

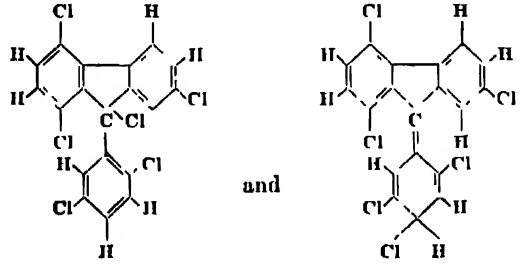
The reaction takes a similar course with *p*-dichlorobenzene, the product in this case being 2,5,2′,5′-tetrachlorobenzophenone chloride:



Like condensations have been found to occur with *o*- and *m*-dichlorobenzene and with *p*-dibromobenzene.[417]

It has been reported that if the reaction of *p*-dichlorobenzene and carbon tetrachloride in the presence of aluminum chloride is conducted in the absence of a solvent at room temperature, a 26 per cent yield of 2,5,2′,5′-tetrachlorobenzophenone is secured; however, if the reaction is effected by heating for ten hours at 55°, two phenylfluorene derivatives, both of them having the composition $C_{19}H_8Cl_6$, are obtained.[415]

These probably had the following structures:



Here the intermediate products may have been halogenated triphenylmethane derivatives which, with hydrogen chloride cleavage, condensed to the fluorenes.

That chlorine in the ring has an inhibiting effect on Friedel-Crafts reaction may be assumed from the fact that, whereas benzene and carbon tetrachloride give a 90 per cent yield of benzophenone chloride[418] with

[416] J. F. Norris and E. H. Green, *Am. Chem. J.*, 26, 492-499 (1901); *J. Chem. Soc. Abs.*, 82 (I), 379 (1902) J. F. Norris and W. C. Twiss, *Am. Chem. J.*, 30, 392-399 (1903); *J. Chem. Soc. Abs.*, 86 (I), 63 (1904).

[417] J. Boeseken, *Rec. trav. chim.*, 27, 5-9 (1908); *J. Chem. Soc. Abs.*, 94 (I), 189 (1908). S. D. Wilson and Y. Cheng, *J. Org. Chem.*, 5, 223-226 (1940).

[418] M. Gomberg and R. L. Jickling, *J. Am. Chem. Soc.*, 37, 2575-2579 (1915); *C. A.*, 10, 53.

p-dichlorobenzene, the yield of the corresponding halogenated derivative is only 26 per cent.[415] Low yields of expected Friedel-Crafts reaction products with halogenated benzenes may be due to formation of such complex polynuclear products as are observed in the formation of fluorene derivatives.

The inhibiting effect of nuclear halogen is evident when yields obtained in the alkylation of diphenyl ether[419] and of halo-diphenyl ethers are contrasted[420] In one case, alkyl halides (C_2 to C_7) condense with diphenyl ether and aluminum chloride to alkylated diphenyl ethers in yields of 96 to 100 per cent, based on the diphenyl ether reacted; whereas in like reactions with halodiphenyl ethers the yields of alkyl-halodiphenyl ethers amount to 45 6 to 68 per cent, based on the halo-diphenyl ether consumed in the reaction.

Phenols

Work which has been done on Friedel-Crafts condensation of phenols with alkyl halides consists primarily of reactions effected with highly active tertiary alkyl halides or the likewise highly active benzyl halides The use of secondary alkyl halides is cited in a few cases, especially in reactions in which the aromatic component is an alkylated phenol or a polynuclear compound. Little information is available concerning condensations of halogenated methane derivatives and phenols in the presence of aluminum chloride.

In 1899, the reaction, in the presence of iron chloride and of aluminum chloride, was investigated by Gurewitsch.[421] With resorcinol, *tert*-butyl chloride and iron chloride, the initial product was the butyl ether of dibutylresorcinol, which was easily converted to *tert*-dibutylresorcinol Using aluminum chloride, however, *tert*-dibutylresorcinol was obtained without isolation of the intermediate ether. In both cases an excess of alkyl chloride was used. The reaction was not regarded as a very suitable method for the preparation of alkylated phenols.

More recently, however, interest in the utilization of alkyl halides, easily obtainable from the great amounts of olefins made available by the petroleum industry, has aroused new interest in the reaction, particularly for the preparation of certain alkylated phenols which find application in the coatings industry[422] and for the preparation of compounds of the thymol group, which are in demand by the perfume industry.[423]

The use of olefins for alkylation of phenols is described in another section of this book.* Literature dealing with the preparation of alkyl phenols by condensation of alkyl halides with phenols is mainly patent

[419] U. S P 2,170,809 (1939) to G H. Coleman and R. P Perkins (to Dow Chemical Co.).
[420] U S P 2,170,989 (1939) to G. H Coleman and R. D. Dreisbach (to Dow Chemical Co)
[421] A Gurewitsch, *Ber.*, 32, 2424-2428 (1899).
[422] U S P 2,049,447 (1936) to H Hönel (to Beck Koller, and Co.); French P 771,214 (1934) to Standard Oil & Development Co.; French P. 689,014 (1930) to Bakelite Corp
[423] U S P 2,064,855 (1936) to M S. Carpenter (to Givaudan-Delawanna, Inc), *C. A.*, 31, 900

* See page 466.

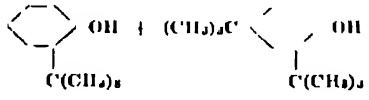
literature which reflects constant attempts at improvement in yields and utilization of by-products.

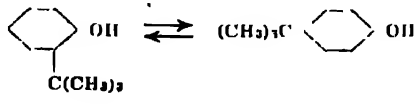
The alkylation of phenol with butyl-, isobutyl-, or isoamyl chlorides has been carried out in the presence of an equimolecular amount of aluminum chloride. The best yields of alkylated products, up to 60 per cent of theory, were obtained in absence of a solvent. Temperatures of about 110° and 4-6 hours of heating were required. Some isomerization of the alkyl group occurred. Formation of alkyl phenyl ethers could not be entirely prevented.[423a].

In reacting a *tert*-alkyl halide such as *tert*-butyl chloride with a phenol having the *o*- and *p*-positions relative to the hydroxy- group free, in the presence of a catalyst such as aluminum chloride, and at temperatures of 50-200°, there is formed the corresponding 4-*tert*-alkylphenolic compound, together with appreciable quantities of the corresponding 2-*tert*-alkylphenolic compound and 2,4-di-*tert*-alkylphenolic compound.[424] Although these last two compounds find industrial application, in order to obtain exclusively the mono-*para* substituent, the 2-*tert*-alkyl- and the 2,4-di-*tert*-alkylphenols may be converted to the desired product by subsequent treatment with aluminum chloride, or by returning the unwanted phenols to the reaction mixture. The general reactions described may be illustrated in the preparation of various *tert*-butylphenols:

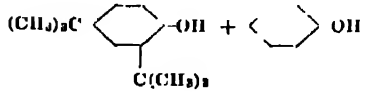
(1) $(CH_3)_3C.Cl + C_6H_5OH \xrightarrow{AlCl_3} (CH_3)_3CC_6H_4OH + HCl$

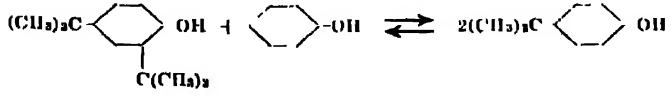
and appreciable quantities of



(2) 

and some



(3) 

[423a] P. Tsukervanik and V. D. Tambovtseva, *Bull. univ. Asie centrale*, 22, 221-5 (1938); *C. A.*, 44, 4729.

[424] U. S. P. 1,972,599 (1934) to R. P. Perkins, A. J. Dietzler, and J. T. Lundquist (to Dow Chemical Co.).

In the initial reaction, approximately equimolecular quantities of *tert*-butyl chloride and phenol are reacted by stirring with aluminum chloride in amount representing about 1 per cent of the weight of phenol used. The reaction was started at about 15°C and the temperature of the mixture was gradually raised to 100° during the course of the reaction. After completion of reaction and upon cooling to 90°, the mixture was agitated with about 4 per cent of its weight of a 50 per cent aqueous sodium carbonate mixture. Filtration and subsequent fractional distillation gave the following products, the yields being expressed as percent of the crude reaction mixture:

2-*tert*-butylphenol, b. 117.1°/23.5 mm. in 1.2% yield
4-*tert*-butylphenol, 70.2% yield
2,4-di-*tert*-butylphenol, b. 147.8°/23.5 mm in 7.1% yield
10% unreacted phenol.

Conversion of 2,4-di-*tert*-butylphenol to 4-*tert*-butylphenol may be effected by heating with phenol in the presence of aluminum chloride The yield of the *p*-derivative amounts to 74.5 per cent of the theoretical, based upon the quantity of 2,4-di-*tert*-butylphenol used.

2-*tert*-Butylphenol may also be added to a reaction mixture consisting of *tert*-butyl chloride, phenol, and aluminum chloride to secure a 74.5 per cent yield of 4-*tert*-butylphenol based on the combined quantities of phenol and 2-*tert*-butylphenol.

Other tertiary alkyl halides, for example, *tert*-amyl bromide or *tert*-hexyl chloride, may be similarly employed as alkylating agents. Other phenolic constituents which may be used in the preparation of *tert*-alkyl phenols are:

3-methylphenol
2,3-dimethylphenol
2,5-dimethylphenol
2,3,5-trimethylphenol
2-ethylphenol
2-chlorophenol
2,5-dichlorophenol
2-isopropylphenol
2-secondary butylphenol, etc.

It has been found that some *tert*-alkyl halide is carried over in the hydrogen chloride vapor when the halide reacts with phenols in the presence of aluminum chloride. This may be recovered by passing the vapors into the *tert*-alcohol corresponding to the *tert*-alkyl halide. The hydrogen chloride is thereby converted into alkyl halide and necessity for the separation of the escaping halide is obviated.[425]

The escaping *tert*-alkyl halide may also be trapped by passage through phenol and a catalyst.[426]

The use of an inert solvent, keeping the reaction mixture fluid at temperature below 50°, is claimed to improve yields of the 4-*tert*-alkyl phenol.[426]

Preliminary gentle heating of the phenol together with the *sec*- or

[425] U. S. P. 1,991,332 (1935) to R. P. Perkins, A. J. Dietzler, and J. T. Lundquist (to Dow Chemical Co.). *Brit. Chem. Abstracts-B*, 91 (1936).
[426] U. S. P. 2,039,344 (1936) to M. E. Putnam, E. C. Britton, and R. P. Perkins (to Dow Chemical Co.). *Brit. Chem. Abstracts-B*, 523 (1937).

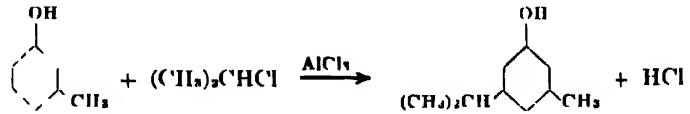
tert-alkyl halide, and subsequent vigorous heating in the presence of the alkylating catalyst, *e.g.*, aluminum chloride in amount less than 3 per cent by weight of the phenol used, has also been suggested.[427]

p-tert-Butylphenol may likewise be prepared by passing isobutylene through a solution of phenol in carbon tetrachloride containing aluminum chloride and a small amount of *tert*-butyl chloride. The alkyl halide present serves to initiate the reaction, and the hydrogen chloride evolved reacts with the incoming olefin to form additional alkyl halide in order to carry on the reaction.[428] The method may also be used for the preparation of isopropylphenol, *p*-tert-amylphenol and *o-tert*-butylnaphthol.[429]

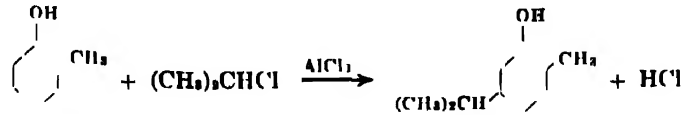
In the preparation of phenols of the thymol group (isopropylcresols) it has been found that the careful control of temperature is a major factor in securing a good yield of the desired isomer, and that chlorinated hydrocarbons such as ethylene dichloride are especially efficient solvents for Friedel-Crafts reactions of this type.[430]

For example, reaction of *m*-cresol with isopropyl chloride at −10° gives thymol as the main product:

Isothymol is produced in only very small yields as a by-product in the foregoing reaction. If, however, the reaction is conducted at 30-60°, and held at 60° for thirty minutes, an almost quantitative yield of 3-methyl-5-isopropylphenol (isothymol) is secured:



Meta-substitution in this case may be explained by a primary formation of the *ortho-para* derivative, thymol, and subsequent rearrangement to 3-methyl-5-isopropylphenol by the action of aluminum chloride.[431] The formation of an *ortho-para* derivative at low temperatures is also demonstrated in the reaction of *o*-cresol with isopropyl chloride at −15° to give carvacrol:



[427] U. S. P. 2,091,483 (1937) to John F. Olin (to Sharples Solvents Corp.).
[428] French P. 697,711 (1930) and Austrian P. 124,281 (1931) to F. Linner (to Soc. Reichhold, Flügand Boecking); *C. A.*, 25, 3018; 26, 735.
[429] U. S. P. 1,892,990 (1933) to F. Linner (to Beck, Koller, and Co.); *C. A.*, 33, 2319.
[430] U. S. P. 2,064,885 (1936) to M. S. Carpenter (to Givaudan-Delawanna, Inc.); *C. A.*, 31, 900
[431] *cf* J. F. Norris and D. Rubinstein, *J. Am. Chem. Soc.*, 61, 1163-1170 (1939).

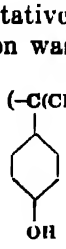
α- or β-Naphthol may be condensed with *tert*-butyl chloride. The naphthol, alkyl halide, and aluminum chloride are mixed at room temperature and warmed gently under a reflux condenser until evolution of hydrogen chloride ceases. The reaction mixture is subsequently boiled with water and distilled under vacuum. β-Naphthol thus yields 4-*tert*-butyl-2-hydroxynaphthalene (m.p. 102° and b.p. 146°/8 mm) and α-naphthol the corresponding 1-hydroxy- derivative.[432]

Alkyl chloro-hydroxy-biphenyls are prepared by reacting a chlorohydroxybiphenyl compound with an alkyl halide in the presence of aluminum chloride.[433] Using one mole each of 2-hydroxy-5-chlorobiphenyl and 2-chloropropane with 0.03 mole of aluminum chloride, a yield of 0.54 mole of 2-hydroxy-3-isopropyl-5-chlorobiphenyl was secured. The products are claimed as microbicides, antiseptics, preservatives, and intermediates.

The aluminum chloride-catalyzed reaction of phenol or cresol with an alkyl halide containing at least 12 carbon atoms for the production of nuclear alkyl derivatives of phenols has been used in preparing materials which, upon sulfonation, yield compounds suitable for use as detergents, foaming agents, and wetting agents.[434]

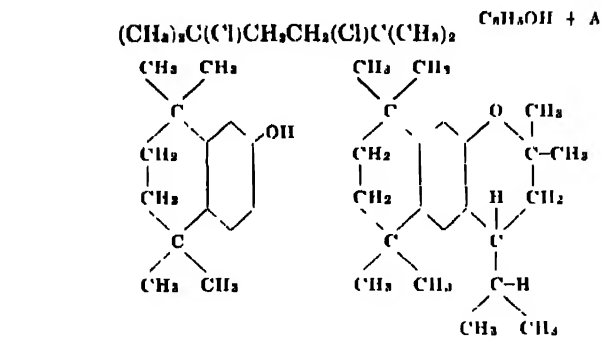
Pour-point depressors for lubricants may be obtained by reacting hydroxy- compounds of the benzene, naphthalene, and anthracene series in the presence of aluminum chloride with chlorinated aliphatic hydrocarbons of not less than 12 carbon atoms, and esterifying the products with a carboxylic acid.[435]

Reacting rubber dibromide with phenol in the presence of aluminum chloride or zinc chloride, 65-77 per cent yields of bis-(hydroxyphenyl) rubber were obtained.[436] With ferric chloride as catalyst, however, the yield was almost quantitative. In a later study of the reaction product the following constitution was indicated[437]:



Di-tertiary, 1,4-dichlorides react with phenols so as to introduce a new hydroaromatic cycle. 2,5-Dichloro-2,5-dimethylhexane and phenol thus give an 80 per cent yield of 5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthol together with a product of higher condensation[438]:

[432] U. S. P. 1,788,529 (1931) to F. Koenigsberger (to Dehls and Steen); *C. Z.*, 1931, II, 1351; *C. A.*, 25, 974.
[433] U. S. P. 2,092,724 (1937) to E. C. Britton, G. H. Coleman, and L. E. Mills (to Dow Chemical Co.).
[434] U. S. P. 2,134,711 (1938) to L. H. Flett (to National Aniline and Chemical Company).
[435] Brit. P 491,328 (1937) to Socony-Vacuum Oil Co.; *Brit. Chem. Abstracts*-B, 1288 (1938). U. S. P. 2,191,498-9 (1940) to O. M. Reiff (to Socony-Vacuum Oil Co.).
[436] H. L. Fisher, H. Gray, and E. M. McColm, *J. Am. Chem. Soc.*, 48, 1309-1312 (1926).
[437] E. Geiger, *Helv. Chim. Acta*, 10, 530-538 (1927); *C. Z.*, 1927, II, 1023-1024.
[438] H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, 62, 38-44 (1940).



Condensation products of phenols with halogenated squalene are prepared by adding squalene hexahydrobromide to a mixture of phenol and aluminum chloride (100:1) at 60-70°, and subsequently heating the reaction mass for eight hours at 80°. Like condensation with squalene dodecabromide yields a product (m.p. 120-130°), which yields dyestuffs with diazo- compounds. Instead of phenol, α-naphthol may be used as the aromatic component.[439]

Although little is known about the reaction of unsaturated alkyl halides with phenols, it has been claimed that the condensation of a vinyl halide with phenols in the presence of aluminum chloride yields vinylphenol.[440]

By condensing *o*-cresol with carbon tetrachloride in the presence of aluminum chloride, and hydrolyzing the product, 3,3′-dimethyl-4,4′-dihydroxybenzophenone has been obtained.[441]

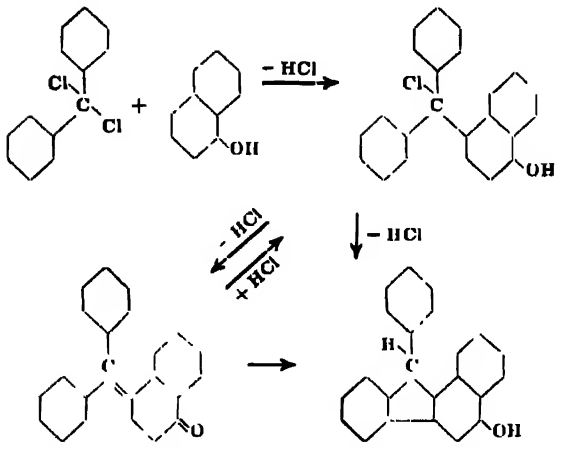
The alkylating agent may be an alicyclic halide. Phenol with *tert*-methylcyclopentyl chloride with aluminum chloride in an indifferent solvent gives a good yield of *p-tert*-methylcyclopentylphenol.[442]

Dipentene dihydrochloride undergoes Friedel-Crafts condensation with phenol and aluminum chloride to give dihydroxydiphenylmenthane.[443]

Aralkyl halides undergo Friedel-Crafts condensation with certain phenols. Benzyl chloride and resorcinol with aluminum chloride give a 50 per cent yield of [2,4-dihydroxyphenyl]phenylmethane (m.p. 76-77°).[444] Condensation of 1 mole each of α-chlorobutylbenzene and phenol in petroleum ether, using ½ mole of aluminum chloride, gives a 20 per cent yield of 4-(α-phenylbutyl)phenol and a 6 per cent yield of 2-(α-phenylbutyl)phenol.[445]

Diphenyldichloromethane with α-naphthol in the presence of aluminum chloride gives a fluorene derivative.[446] The condensation has been shown to proceed according to the scheme:

[439] Brit. P. 345,784 (1931); French P. 709,862 (1931) to H. M. Bunbury and W. A. Sexton (to Imperial Chemical Industries); *C. Z.*, 1931, II, 771.
[440] U. S. P. 2,006,517 (1935) to G. W. Seymour (to Celanese Corporation); *C. A.*, **29**, 5458.
[441] Brit. P. 417,519 (1934) to British Celanese, Ltd.
[442] U. S. P. 2,102,172 (1936) to H. Hönel and A. Zinke (to H. Reichhold).
[443] French P. 790,206 (1936) to Soc. francaise Becknerite; *C. A.*, **30**, 5684.
[444] E. Klarmann, *J. Am. Chem. Soc.*, **48**, 791-794 (1926).
[445] R. C. Huston and H. W. Strinkler, *J. Am. Chem. Soc.*, **55**, 4317-4318 (1933); *Brit. Chem. Abstracts-A*, 1287 (1933).
[446] E. Clar, *Ber.*, **63**, 512-517 (1930); *C. A.*, **24**, 3007.



3-Hydroxy-9-phenyl-1,2-benzofluorene is thus obtained in almost quantitative yield.

An extensive study of the influence of halogen substituents on the course of the reaction with benzyl chloride has been made by Huston and co-workers.[447] Condensations were carried out with one mole of the benzyl chloride and 3 moles of the phenol in the presence of ½ mole of aluminum chloride at 20-35°. Diphenylmethane derivatives are obtained, the condensation taking the normal course, with replacement only of the methylenic halogen. Reactions with chloro- derivatives are summarized:

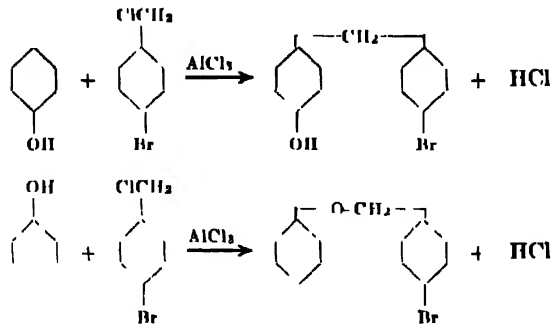
Phenol	Chloride	Derivative of diphenylmethane	% yield
Phenol	2-chlorobenzyl	{2-hydroxy-2'-chloro- {4-hydroxy-2'-chloro-	16.21 14.74
Phenol	3-chlorobenzyl	4-hydroxy-3'-chloro-	15.84
Phenol	4-chlorobenzyl	4-hydroxy-4'-chloro-	46.00
2-Chlorophenol	benzyl	{2-hydroxy-3-chloro- {4-hydroxy-3-chloro-	
4-Chlorophenol	benzyl	2-hydroxy-5-chloro-	
2,6-Dichlorophenol	2-chlorobenzyl	4-hydroxy-3,5,2'-trichloro-	16.8
2,6-Dichlorophenol	3-chlorobenzyl	4-hydroxy-3,5,3'-trichloro-	11.52
2,6-Dichlorophenol	4-chlorobenzyl	4-hydroxy-3,5,4'-trichloro-	35.00

Substitution in the *ortho*-position to the hydroxy occurred only in the reactions of phenol with 2-chlorobenzyl chloride, and 2-chlorophenol with benzyl chloride. With 2,6-dichlorophenol and 2-chlorobenzyl chloride, of course, only the *para*- derivative was obtained.

Condensations with brominated derivatives showed that the presence of bromine in the nucleus of benzyl chloride favors the formation of an ether. Thus phenol with 4-bromobenzyl chloride yielded not only the

[447] For work with chlorine substituents see R. C. Huston, R. L. Guile, P. S. Chen, W. N. Headley, L. W. Warren, L. S. Bauer, and B. O. Mata, *J. Am. Chem. Soc.*, **55**, 4630-4643 (1933); for work with bromine substituents see R. C. Huston, A. Neeley, B. L. Fayerweather, H. M. D'Arcy, F. H. Maxfield, M. M. Ballard, and W. C. Lewis, *J. Am. Chem. Soc.*, **53**, 2146-2149 (1933).

expected diphenylmethane derivative but also 4-bromobenzyl phenyl ether:



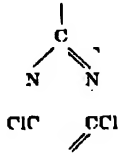
Preparations with brominated derivatives are given:

Phenol	Chloride	Products
Phenol	2-bromobenzyl	4-hydroxy-2'-bromodiphenylmethane—15% yield 2-hydroxy-2'-bromodiphenylmethane 2-bromobenzyl phenyl ether
Phenol	3-bromobenzyl	4-hydroxy-3'-bromodiphenylmethane—17% yield 3-bromobenzyl phenyl ether
Phenol	4-bromobenzyl	4-hydroxy-4'-bromodiphenylmethane—19% yield 4-bromobenzyl phenyl ether

The benzylation of a bromophenol did not give an ether. The production of *ortho*-benzyl derivatives occurs as it did in reactions with chloro-substituted compounds.

Chlorine-substituted benzyl chloride may be reacted with phenols to yield water-soluble condensation products which find use in the textile industries. An aromatic hydroxy- compound such as phenol is heated with about the same quantity of a halogenated aralkyl halide containing no hydroxyl group, such as trichlorobenzyl chloride, at a temperature of 100° or lower for three to fifteen hours, in the presence of zinc chloride or aluminum chloride, and the condensation product thus obtained is sulfonated at a temperature of 35-80° to obtain a product which may be used as a resin in treating fabrics, etc.[448]

Several instances cite the condensation of phenols with halogenated ring compounds of nitrogen. Cyanuryl chloride,



[448] U. S. P. 1,948,430 (1934) to General Aniline Works; *C. A.*, **28**, 2367. *cf.* British P. 430,592 (1935) to I. G. Farbenindustrie; *C. A.*, **32**, 6359.

condenses with α-naphthol in the presence of aluminum chloride with replacement of halogen by the naphthol residue.[449] Replacement of halogen by phenol- or naphthol-residues also takes place in the reaction of 2- or 4-halogeno- or 2,4-dihalogeno-quinazolines and phenol or naphthols in the presence of aluminum chloride.[450]

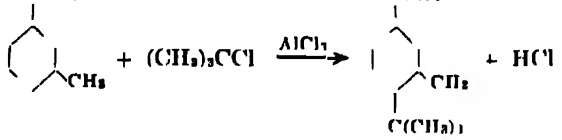
Other chlorinated triazines have been claimed to undergo like reactions with naphthols [451] or phenols.[452]

Phenol Ethers

Condensation of phenol ethers with acyl halides in the presence of aluminum chloride is so generally used that reactions of this type make up a substantial part of the chapter on Friedel-Crafts reactions with acyl halides.* Although many other halogenated compounds condense with phenol ethers and aluminum chloride with replacement of halogen by the phenoxy- group, the data available concerning yields and speed of reaction are not sufficiently comprehensive to allow generalizations concerning the influence of the alkoxy- group in Friedel-Crafts alkylations. However, the fact that methyl anisate and anisaldehyde alkylate smoothly, whereas methyl benzoate and benzaldehyde do not undergo the reaction, indicates an activating effect of the alkoxy- group.

Upon heating anisole with aluminum chloride and isobutyl bromide or *tert*-butyl chloride, Baur [453] obtained methyl (4-*tert*-butylphenyl) ether, $(CH_3)_3C.C_6H_4.O.CH_3$. Treatment of *m*-tolyl methyl ether with the same alkyl halides and aluminum chloride gave the tertiary butyl derivative, $(CH_3)_3C.(C_6H_3).CH_3.O.CH_3$, (b. 222-224°). The best yields were obtained when 5 parts of the cresyl ether were used with 1 part of butyl bromide and 0.2-0.1 part of aluminum chloride.

The condensation of *m*-tolyl methyl ether with *tert*-butyl chloride at a low temperature in the presence of only a very small amount of aluminimum chloride has been shown more recently [454] to result only in the formation of 4-*tert*-butyl-*m*-tolyl methyl ether (m.p. 23.4°):



[449] U. S. P. 1,734,029 (1929) to American Cyanamid Corp.; *C. Z.*, 1930, I, 740.

[450] British P. 287,179 (1928) to I. G. Farbenindustrie, *Brit. Chem. Abstracts*-B, 717 (1929).

[451] Swiss P. 108,191-108,202 (1924); Brit. P. 220,302 (1923); French P. 584,043 (1923) to Soc. f. chem. Ind. in Basel; *C. Z.*, 1925, II, 780-781.

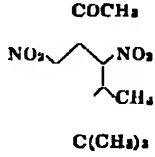
[452] German P. 459,100 (1926); British P. 240,371 (1925) to Soc. f. Chem. Ind. in Basel; *C. Z.* 1926, II, 2117.

* See page 308.

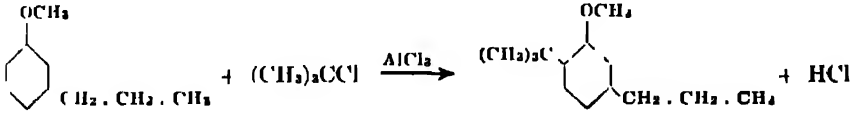
[453] A. Baur, *Ber.*, 27, 1618-1619 (1894). For later work on reaction of anisole with butyl-, isobutyl or isoamyl chloride to give up to 70 per cent yields of monoalkylation products see I. P. Tsukervanik and V. D. Tambovtseva *Bull. univ. Asie Centrale*, 22, 221-5 (1938); *C. A.*, 34, 4729.

[454] G. Darzens and A. Levy, *Compt. rend.*, 193, 331-334 (1931); *C. Z.*, 1931, II, 2319.

The structure of the product was determined by nitration to amber musk, or by acetylation to the known acetyl derivative.[455]



Good results have been secured in Friedel-Crafts alkylation of 3-propylanisole. From 15 g of the ether, 9.2 g of *tert*-butyl chloride, and 3.2 g of aluminum chloride, there is obtained 12.5 g of 3-propyl-6-*tert*-butyl anisole acccording to the scheme[456]:



It will be noted that here the orientation of the entering alkyl group differs from that reported in the reaction of *tert*-butyl chloride with *m*-tolyl methyl ether noted above.

Ethers of polynuclear hydrocarbons may be alkylated by Friedel-Crafts condensation with alkyl halides. When 100 g of isobutyl bromide are reacted with a mixture of 96 g of β-naphthyl methyl ether and 81 g of aluminum chloride in 192 g of carbon disulfide at 55-65°, and the reaction mixture is fractionated under vacuum, isobutylnaphthyl methyl ether (m.p. 66°, b.p. 188°/14 mm), is obtained.[457]

Alkylated diphenyl ethers, produced by condensation of diphenyl ether with alkyl halides in the presence of aluminum chloride, have been claimed as products particularly valuable as dielectric agents in transformers, condensers, and other electrical equipment, or as plasticizers for resins and varnishes.[458] Upon treating a mixture consisting of 10 moles of diphenyl ether and 0.2 mole of aluminum chloride with 10.06 moles of ethyl chloride at approximately 150° during a fourteen-hour period, a mixture of ethylated diphenyl ethers was obtained. Based on the diphenyl oxide reacted, the yields of products obtained were as follows:

monoethyldiphenyl ethers	58%
diethyldiphenyl ethers	30%
triethyldiphenyl ethers	10%
tetraethyldiphenyl ethers	2%

Condensation of secondary butyl chloride with diphenyl ether at 100° for 2½ hours gave the following products in the indicated yields:

[455] J. H. Barbier, *Helv. Chim. Acta*, 11, 152-156; *C. Z.*, 1928, 1, 1397.
[456] S. G. Cousin and F. Lions, *J. Proc. Roy. Soc. N. S. Wales*, 70, 413-427 (1937); *C. A.*, 31, 6637.
[457] L. Cahen, *Bull. soc. chim. (3)*, 19, 1007-1008 (1898); *C. Z.*, 1899, 1, 287.
[458] U. S. P. 2,170,809 (1939) to G. H. Coleman and R. P. Perkins (to Dow Chemical Co.)

mono-*sec*-butyldiphenyl ethers	71%
di-*sec*-butyldiphenyl ethers	24%
tri-*sec*-butyldiphenyl ethers	5%

Like reactions were effected also with the diphenyl ethers and *tert*-butyl chloride, *tert*-amyl chloride, isomeric amyl chlorides derived from the chlorination of pentane, hexyl chlorides, bromides or iodides, and heptyl halides. The reaction is likewise applicable to condensation of alkylated diphenyl oxides with alkyl halides.

Alkyl halo-diphenyl ethers obtained by reaction of chlorodiphenyl ethers with alkyl halides of from 1 to 6 carbon atoms have also been claimed for use as dielectric agents and as plasticizers.[459] Condensation of 8.6 moles of ethyl chloride with 9.0 moles of crude monochlorodiphenyl ether in the presence of 0.2 mole of aluminum chloride for six hours at 150° gave the following yields of alkylated products, based on reacted chlorodiphenyl ether:

monoethyl chlorodiphenyl ether	32.4%
diethyl chlorodiphenyl ether	6.7%
polyethyl chlorodiphenyl ether	6.5%

With *tert*-butyl chloride and aluminum chloride at 85-95° for 3½ hours, chlorodiphenyl ether gave a 52.4 per cent yield of mono-*tert*-butylchlorodiphenyl ether and a 15.8 per cent yield of the corresponding di-alkyl derivative.

Dichlorodiphenyl ether with *sec*-butyl chloride gave at 90-95° for 0.83 hour a 48.2 per cent yield of mono-*sec*-butyl dichlorodiphenyl ether and an 18.5 per cent yield of di-*sec*-butyl dichlorodiphenyl ether.

On the whole, it is obvious that better conversion is obtained in Friedel-Crafts condensation of unhalogenated diphenyl ether with alkyl halides than when the halogenated ether is used as the aromatic component.[458]

The reaction of diphenyl ether with dihalo-aliphatic hydrocarbons and aluminum chloride at 145-250° results in the formation of mixtures of such compounds as the isomeric *bis*-(phenoxyphenylethyl)diphenyl ethers, the isomeric *bis*-(phenoxyphenylpropyl)diphenyl ethers, and different mixtures of the isomeric *bis*-(phenoxyphenylbutyl)diphenyl ethers. These phenoxyphenylalkyl diphenyl ethers are obtained by heating an excess of the ether with the alkyldihalide and a small proportion of aluminum chloride. Thus by reacting 4 moles of diphenyl ether with 1 mole of ethylidene dichloride and 0.1 mole of aluminum chloride for five hours at 200°, a mixture consisting of mono- and di-(phenoxyphenylethyl)diphenyl ether is obtained. The products may be used as plasticizers and as lubricant addition agents.[460]

Substances resembling lubricating oils are claimed to be products of the reaction of halogenated aliphatic hydrocarbons having more than 12 carbon atoms in the presence of a Friedel-Crafts catalyst with an aro

[459] U. S. P. 2,170,989 (1939) to G. H. Coleman and R. D. Dreisbach (to Dow Chemical Co.)
[460] U. S. P. 2,079,279 (1937) to G. H. Coleman and B. C. Hadler (to Dow Chemical Co.). *C* 4 31, 4416.

matic ether free from amino-, nitro-, carboxylic acid, aldehyde, hydroxy-, or sulfonic groups or halogens, having a free nuclear position.[461] Examples are given of the condensations of chlorinated paraffin wax with

anisole
diphenylene oxide
diphenyl ether
dinaphthyl ether
β-naphthyl ethyl ether
cyclohexyl phenyl ether
α-naphthyl methyl ether
dinaphthylene oxide.

The alkylation of products obtained by condensing aryl-aryl, alkyl-aryl, aralkyl-aryl, and aralkyl ethers with chlorinated petroleum wax in the presence of aluminum chloride is said to result in improved pour-point depressors.[462]

There are cited only a few instances of Friedel-Crafts reactions of ethers with halogenated compounds other than alkyl or acyl halides.

In attempted condensation of anisole with carbon tetrachloride and aluminum chloride, it was observed that only traces of the corresponding dimethoxybenzophenone were obtained.[463] It was assumed that the negative results were due to the formation of a resistant additive product of anisole and aluminum chloride.

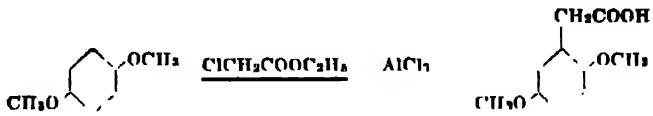
The action of bromonitromethane and aluminum chloride on anisole has been investigated.[464] Two types of reactions occurred: the halogen was replaced by the anisyl group in one, and in the other the nitroalkyl-halide acted as a brominating agent. Only a very small amount of the product from the former reaction was obtained, and this tended largely to decompose into aldehyde and acid.

The condensation of benzyl chloride with anisole has been effected by boiling the components for two or three hours in the absence of a catalyst. The product is *p*-methoxydiphenylmethane.[465] The same compound may be obtained even at 0° if the reaction is conducted in the presence of aluminum chloride.[466] According to Nenitzescu and co-workers[465] the presence of aluminum chloride only allows the use of lower temperatures in the reaction.

Treatment of 90 g of veratrole in 200 cc of carbon disulfide with 20 g of aluminum chloride and 50 g of benzal chloride has been reported to yield 58 g of phenyldiveratrylmethane (m.p. 124°), together with some 9,10-diphenyl-2,3,6,7-tetramethoxy-9,10-dihydroanthracene (m.p. 308°) as the non-volatile residue.[467] Here replacement of both halogens from the benzal chloride by the veratryl residues had occurred.

[461] British P. 440,916 (1936) to The Resinous Products & Chemical Co.; *C.*, **30**, 4314.
[462] U. S. P. 2,114,812 (1938) to O. M. Reiff and D. E. Badertscher (to Socony-Vacuum Oil Company).
[463] J. Boeseken, *Rec. trav. chim.*, **24**, 1-5 (1905); *J. Chem. Soc. Abs.*, **88** (I) 423 (1905).
[464] M. L. Sherrill, *J. Am. Chem. Soc.*, **46**, 2752-2758 (1924); *C. A.*, **19**, 481.
[465] C. D. Nenitzescu, D. A. Isacescu, and C. N. Ionescu, *Inst.*, 491, 210-220 (1931); *C. A.*, **26**, 1257.
[466] H. Goldschmidt and H. Larsen, *Z. physik. Chem.*, **48**, 424-434 (1904).
[467] J. N. Graves, G. K. Hughes, and F. Lions, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 318-322 (1938) (reprint); *C. A.*, **33**, 571.

Hydroquinone dimethyl ether has been reacted with ethyl chloroacetate and aluminum chloride by boiling in a reflux apparatus for three to five days to give the dimethyl ether of homogentisic acid:



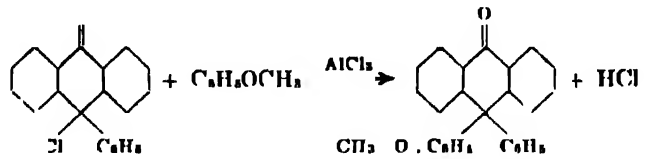
Saponification of the ester occurred during the reaction; otherwise normal Friedel-Crafts condensation took place.[468]

A similar reaction could not be effected with anisole and chloromethylene dibenzoate in the presence of aluminum chloride. Wenzel and Bellak [469] expected that condensation would occur according to the scheme:

$$(C_6H_5CO_2)_2CHCl + C_6H_5OCH_3 \qquad (C_6H_5CO_2)_2CHC_6H_4OCH_3 + HCl$$

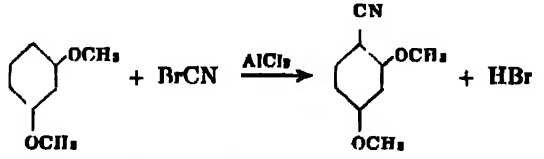
Instead of the dibenzoate, however, the reaction product was found to be anisaldehyde, which may have been produced through intermediate formation of anisaldehyde dibenzoate.

The condensation of anisole with chlorophenylanthrone in carbon disulfide in the presence of aluminum chloride yields methoxydiphenylanthrone, m.p. 180-181°:



Ethoxydiphenylanthrone (m.p. 159-160°) is prepared similarly.[470]

The production of nitriles by condensation of freshly prepared cyanogen bromide with aromatic compounds in the presence of aluminum chloride proceeds more readily with phenol ethers than it does with aromatic hydrocarbons.[471] 2,4-Dimethoxybenzonitrile is produced in good yield according to the scheme:

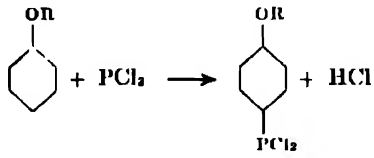


[468] W. A. Osborne, *Proc. Physiol. Soc.* (1903), xiii-xiv; *J. Physiol.*, 29; *J. Chem. Soc. Abs.*, 84 (I), 487 (1903).
[469] F. Wenzel and L. Bellak, *Monatsh.*, 35, 965-971 (1914); *J. Chem. Soc. Abs.*, 108 (I), 534 (1915); *C. Z.*, 1915, I, 136.
[470] L. Tetry, *Compt. rend.*, 128, 1406-1407 (1899); *J. Chem. Soc. Abs.*, 76 (I), 518 (1899).
[471] P. Karrer, A. Rebmann, and E. Zeller, *Helv. Chim. Acta*, 3, 261-272 (1920); *J. Chem. Soc. Abs.*, 118 (I), 389 (1920).

Nitriles of 2,5-dimethoxy-, 3,4-dimethoxy-, 2,3,4-trimethoxybenzene and 4-ethoxy- and 2-methoxynaphthalene were similarly prepared.

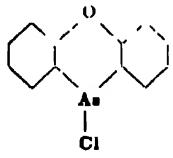
The condensation of phenol ethers and halogenated triazines in the presence of aluminum chloride, with replacement of halogen by the aryloxy- residue, has been claimed to give products useful in the dyestuffs industry.[472]

Phosphorus trichloride condenses with anisole or with phenetole in the presence of aluminum chloride to yield *p*-anisyl or phenetyl chlorophosphine according to the scheme [473]:



With diphenyl ether, *p*-phenoxyphenyldichlorophosphine is similarly obtained.[474]

Arsenic trichloride condenses with diphenyl ether and aluminum chloride to yield 6-chlorophenoxarsine [475]:



A similar condensation occurs when phenyl-α-naphthyl ether is substituted for diphenyl ether in the foregoing reaction, the product in this case being 7-chloro-α-β-naphthaphenoxarsine.[476]

Of interest is the fact that although the aldehyde group has an inhibiting effect in Friedel-Crafts reactions, anisaldehyde with isopropyl chloride and aluminum chloride in carbon disulfide has been reported to give a 22.4 per cent yield of 3-isopropyl-4-methoxybenzaldehyde.[477] Here the methoxy- group obviously has an activating influence on the condensation, for benzaldehyde does not undergo the reaction.

The activating action of the methoxy- group is also apparent in the alkylation of methyl anisate with isopropyl chloride and aluminum chloride.[478]

[472] German P. 433,100 (1926); British P. 240,371 (1925) to Soc. f. chem. Ind. in Basel; *C. Z.*, 1926, II, 2117.

[473] A. Michaelis, *Ann.*, 293, 193-325 (1896), 294, 1-55 (1897). G. Kamai, *J. Gen. Chem. (U.S.S.R.)*, 4, 192 193 (1934); *C. A.*, 29, 464.

[474] W. Cule Davies and Colin J. O. R. Morris, *J. Chem. Soc.*, (1932), 2880-2883; *C. A.*, 27, 966.

[475] W. Lewis, C. D. Lowry, and F. H. Bergeim, *J. Am. Chem. Soc.*, 43, 891-896 (1921).

[476] J. A. Aeschlimann, *J. Chem. Soc.*, 127, 811-815 (1925)

[477] H. Gilman and R. R. Burtner, *J. Am. Chem. Soc.*, 57, 909-912 (1935); *C. A.*, 29, 4354.

[478] H. Gilman and N. O. Calloway, *J. Am. Chem. Soc.*, 55, 4197-4205 (1933); see also p. 193.

Ketones

The keto- group has an inhibiting effect in Friedel-Crafts reactions, but as the aromaticity of a ketonic compound and the activity of the halogen component are increased, condensation becomes possible. This is especially apparent in acylations;* but for alkylation, instances which illustrate this generalization are less common.

Benzoylnaphthalene has been reacted with benzyl chloride.[479] Treatment of 50 g of 1-benzoylnaphthalene and 21.8 g of benzyl chloride with 0.25 g of aluminum chloride in small portions at 160-170° for one hour produces 1-benzoyl-8-benzylnaphthalene, distilling at 290-305°/3-15 mm, and melting at 142° upon crystallization from alcohol.

The amino- group imparts increased aromaticity to the ketonic component. Anilides readily undergo condensation with alkyl halides in the presence of aluminum chloride.[480]

The condensation of 4-aminoanthraquinoneacridone with α-chloroanthraquinone and aluminum chloride to give 4-α-anthraquinonylaminoanthraquinone-1,2-acridone is another instance of such influence.[481]

Alkylation of ketones of the furan series may be effected by reaction with alkyl halides in the presence of aluminum chloride. 2-Furyl phenyl ketone has thus been shown to condense with *tert*-butyl chloride to give a 30 per cent yield of 5-*tert*-butyl-2-furyl phenyl ketone.[482]

In an attempted alkylation of acetophenone, molecular amounts each of acetophenone and ethylbromide were treated with ½ mole of aluminum bromide. Here the main reaction product was methylstilbyl phenyl ketone, $C_6H_5.C(CH_3):CHCO.C_6H_5$, obviously a condensation product of two moles of acetophenone. The ethyl bromide served only as a solvent for the condensation. As a by-product triphenylbenzene was obtained, if a smaller amount of ethyl bromide is used and the reaction temperature increased, greater amounts of triphenylbenzene are produced. It is suggested that the formation of this kind of hydrocarbon and unsaturated ketone almost always occurs in Friedel-Crafts ketone synthesis, if the reaction temperature is high and too much aluminum chloride or aluminum bromide is used.[483]

Acetophenone and chloralhydrate combine by means of aluminum chloride even in the cold, yielding a complex from which aluminum cannot be entirely removed. Vacuum distillation gives decomposition products.[484]

Esters

The carboxy group in the ring has an inhibiting effect in Friedel-Crafts alkylations. However, the presence of a highly activating group

* See page 360.

[479] K. Dziewonski, J. Auerbach, and J. Moszew, *Bull. intern. acad. polonaise*, **1929A**, 658-668; *C. A.*, 25, 1515.

[480] U. S. P. 2,092,970, *C. A.*, 31, 7804; 2,092,972-3, *C. A.*, 31, 7888, to B. Herstein (to U. S. Industrial Alcohol); see also page 197.

[481] German P. 262,252 to Farbwerke vorm Meister, Lucius, and Brüning, *J. Chem. Soc. Abs.*, 104 (I), 1073 (1913).

[482] H. Gilman and N. O. Calloway, *J. Am. Chem. Soc.*, 55, 4197-4205 (1933).

[483] M. Konowalow and Finogejew, *J. Russ. Phys.-Chem. Soc.*, 34, 944-949 (1903); *C. Z.*, 1903, I, 521.

[484] G. B. Frankforter and W. Kritchevsky, *J. Am. Chem. Soc.*, 36, 1525 (1914).

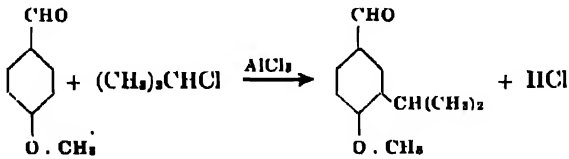
may make alkylation possible. Thus, although methyl benzoate does not undergo Friedel-Crafts reaction with alkyl halides, methyl anisate does. A 33.6 per cent yield of methyl 3-isopropyl-4-methoxybenzoate (b.p. 162-165°/25 mm) has been secured by condensing methyl anisate with isopropyl chloride in the presence of aluminum chloride in carbon disulfide.[485] The methoxy group thus increases the aromaticity of the ester to such an extent that condensation occurs.

The effect of increased aromaticity is also emphasized in alkylations of naphthoates. Ethyl α-naphthoate has been reacted with isopropyl chloride and aluminum chloride to give a 33 per cent yield of ethyl isopropyl-α-naphthoate, b.p. 198-203°/20 mm. With *n*-butyl chloride an ethyl butyl-α-naphthoate has been likewise secured.[485]

Furan esters alkylate readily. Although methyl and ethyl halides cannot be used as alkylating agents, almost quantitative yields can be obtained with propyl and butyl halides [486] and good yields with amyl and hexyl halides.[485] The condensations, effected in yields of up to 66 per cent, imply superaromatic properties for furan.[487]

Aldehydes

The presence of an aldehyde group in the ring has an inhibiting effect on the Friedel-Crafts reaction. From 21.2 g of benzaldehyde, 15.6 g of isopropyl chloride, and 53.2 g of aluminum chloride, only 2.2 g of *m*-isopropylbenzaldehyde (b.p. 95-97°) has been obtained. If, however, a highly activating substituent is also present in the ring, a much better yield is obtained. Treatment of 13.6 g of anisaldehyde with 7.8 g of isopropyl chloride and 26.6 g of aluminum chloride gives 4 g, or a 22.4 per cent yield, of 3-isopropyl-4-methoxybenzaldehyde.[488]



Alkyl derivatives of furfural are obtained by condensation of furfural with alkyl halides.*

Compounds of Nitrogen

Aluminum chloride has been little used for the alkylation of compounds of nitrogen. It has been found useful in reaction of amides with alkyl halides, and it has had a limited application in condensations of arylamines with a number of halogenated compounds. A few isolated

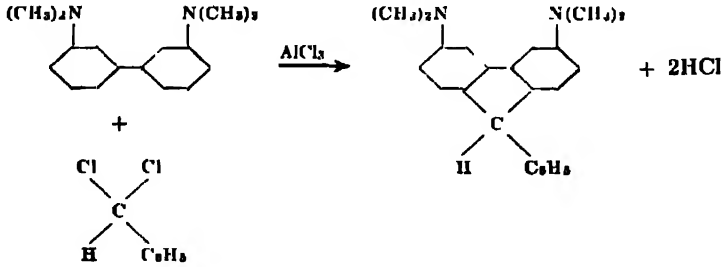
[485] H. Gilman and N. O. Calloway, *J. Am. Chem. Soc.*, 55, 4197-4205 (1933).
[486] N. O Calloway, *Chem. Reviews*, 17, 34 (1935).
[487] H. Gilman and N. O. Calloway, *loc. cit.*; for a discussion of these reactions, see page 200 of this book
[488] H. Gilman and R. R. Burtner, *J. Am. Chem. Soc.*, 57, 909-912 (1935); *C. A.*, 29, 4354.
* See page 202 for a discussion of this reaction.

cases cite its use in reactions effected with heterocyclic compounds of nitrogen. Although Friedel-Crafts reactions of nitrogen ring compounds with acyl halides have been reported,† similar condensations do not occur with alkyl halides. This is also true of nitro compounds; whereas nitro compounds containing highly activating groups do undergo Friedel-Crafts reactions with acyl halides;‡ like condensations with alkyl halides have not been reported.

Nitro compounds.—The nitro group has a decidedly inhibiting effect on Friedel-Crafts alkylation. Nitrobenzene undergoes a reduction-chlorination reaction with isopropyl bromide or isobutyl bromide and aluminum chloride.[489] A solution of 4 moles of nitrobenzene and 0.5 mole of isobutyl bromide was treated with 1 mole of aluminum chloride, cooled, and allowed to stand for thirty days. From the reaction product was obtained the unused nitrobenzene, 10 g of *o*-chloroaniline and 8 g of *p*-chloroaniline. In a similar experiment in which the reaction mixture was heated at 65-75° for 6½ hours, and then allowed to stand for three days at room temperature, there was isolated 11 g of *o*-chloroaniline and 4.5 g of *p*-chloroaniline. In an analogous experiment with isopropyl bromide, 1.5 g of a mixture of *o* and *p*-chloroanilines was secured. With ethyl or methyl bromide only unchanged nitrobenzene was obtained.

In an attempt to prepare nitrothianthrene from nitrobenzene, sulfur chloride, and aluminum chloride, only a black, carbonaceous product was obtained from which no well characterized compound could be isolated.[490] On the other hand, benzene and sulfur chloride with aluminum chloride smoothly react to yield thianthrene (see p. 163).

Aryl amines.—Benzal chloride condenses with 3,3′-tetramethyldiaminobiphenyl and aluminum chloride with replacement of both chlorine atoms to give 3,6-tetramethyldiamino-9-phenyl fluorene[491]: With



1 mole of the amine and 1 mole of the halide, 2 moles plus 10 per cent excess of aluminum chloride was used. The condensation was effected by heating under reflux for about six hours.

† See page 386.
‡ See page 379.
[489] H. Gilman, R. R. Burtner, N. O. Calloway, and J. A. V. Turck, Jr., *J. Am. Chem. Soc.*, 57, 907-908 (1935).
[490] K. Ross, Dissertation, Marburg 1913, p. 34.
[491] S. Duth, *J. Chem. Soc.*, 1171-1184 (1926).

Dialkylanilines condense with benzanilidimido chloride to give halogen replacement products which, upon hydrolysis, give the corresponding dialkylaminobenzophenones.[402] The condensation proceeds:

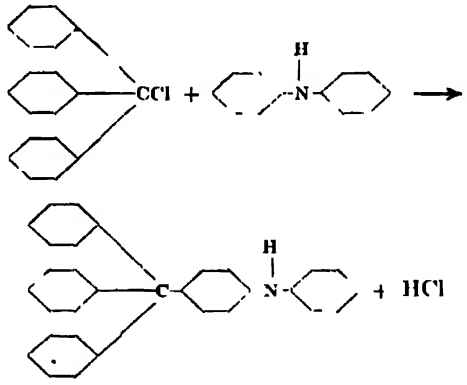
$$R_2NC_6H_5 + C_6H_5 . CCl : N . C_6H_5 \xrightarrow[-HCl]{AlCl_3}$$

$$C_6H_5 . C(:N\ C_6H_5) . C_6H_4 . NR_2 \xrightarrow{H_2O} C_6H_5 . CO . C_6H_4 . NR_2 + NH_2C_6H_5$$

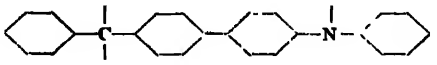
Dimethylamino-, diethylamino-, 4'-nitro-4-dimethylamino-, 4'-nitro-4-diethylamino-, and 4'-bromo-4-dimethylamino-benzophenones were thus obtained in 80, 70, 50, 50, and 70 per cent yields, respectively.

The reaction has also been applied to the production of ketones from dimethyl-*o*-,-*m*-, and -*p*-toluidine, diethyl-*o*-toluidine, dimethyl-α-naphthylamine, benzylmethylaniline, and benzylethylaniline. Dry ether is a better solvent for the reaction than is carbon disulfide.[403]

When triphenylchloromethane is condensed with diphenylamine in the absence of a catalyst, 4-anilino-tetraphenylmethane (m.p. 242°), is obtained [404]



If the condensation is effected in the presence of aluminum chloride, however, the reaction takes a different course. In this case a diarylamine (m.p. 350°), probably of the following structure, is secured:

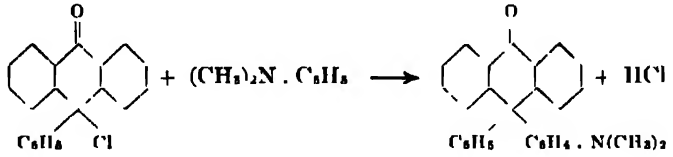


The substance is believed to be *p*-diphenylmethyl-*p'*-phenylaminobi-

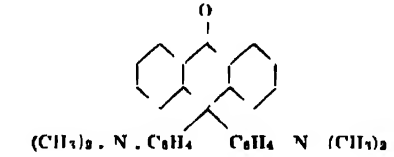
[402] R. C. Shah and J. S. Chaubal, *J. Chem. Soc.*, 650-652 (1932).
[403] R. C. Shah and M. B. Ichhaporia, *J. Chem. Soc.*, 894-896 (1935).
[404] H. Wieland, B. Dolgow, and T. J. Albert, *Ber.*, 52, 898-898 (1919).

phenyl, and has been claimed for use as rubber antioxidant.[495] Similar products may be obtained from other triarylmethyl halides, such as tritolylmethyl chloride or tris (diphenylmethyl) chloride, when caused to react in the presence of aluminum chloride with diarylamines such as diphenylamine, phenyltolylamine, phenylnaphthylamine, or phenylxenylamine. The reaction is not limited to diarylamines, for dialkylanilines undergo like condensation. The products may be used as dye intermediates or antioxidants.[496]

The condensation of dimethylaniline with chlorophenylanthrone in carbon disulfide solution in the presence of aluminum chloride gives dimethylaminodiphenylanthrone (m.p. 215°) according to the scheme

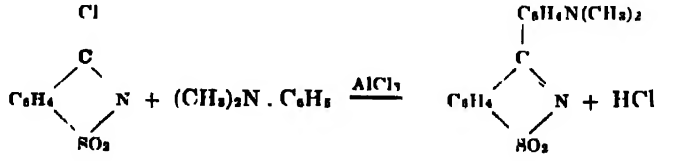


Diethylaminodiphenylanthrone is secured similarly.[497] The chloride of anthraquinone undergoes like reaction with dimethylaniline to give tetramethyldiaminodiphenylanthrone, m.p. 278°:



Tetraethyldiaminodiphenylanthrone (m.p. 218°) is also prepared with ease in a similar manner.[498]

Dimethylaniline has been condensed with 3-chloro-1,2-benzisothiazole-1-dioxide (pseudosaccharinic chloride) in the presence of aluminum chloride to give a normal chlorine-replacement product, 3-(dimethylanilino)-1,2-benzisothiazole-1-dioxide (m.p. 221°), probably according to the scheme[499]:

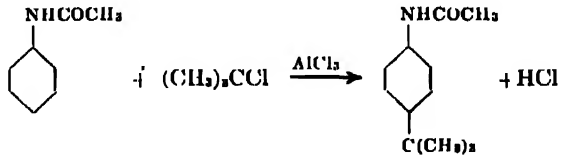


The condensation of dialkylanilines with 9-chloroacridine in the pres-

[495] U. S. P. 1,902,115 (1933) to A. W. Campbell (to B. F. Goodrich Co.); *Brit. Chem. Abstracts*-B, 1070 (1933).
[496] U. S. P. 1,950,079 (1934) to A. W. Campbell (to B. F. Goodrich); *C. A.*, 28, 3079.
[497] L. Tetry, *Compt. rend.*, 128, 1406-1407 (1899); *J. Chem. Soc. Abs.*, 76 (I), 818 (1899).
[498] A. Haller and A. Guyot, *Compt. rend.*, 136, 535-537 (1903); *J. Chem. Soc. Abs.*, 84 (I), 348 (1903).
[499] P. Fritsch, *Ber.*, 29, 2290-2301 (1896).

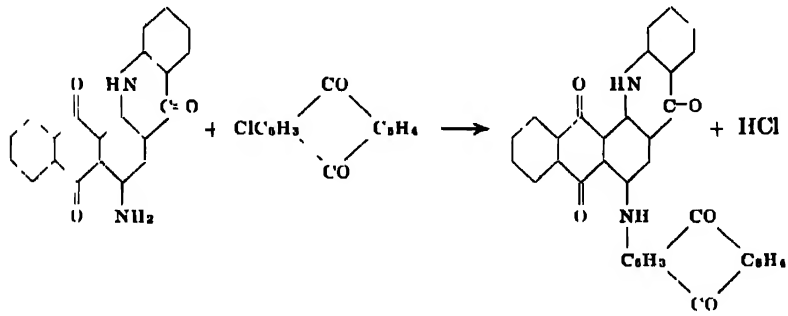
ence of aluminum chloride results in formation of 9-(dialkylaminophenyl) acridines.[500]

Aryl amides.—The alkylation of N-acyl derivatives of aromatic amines takes place readily in the presence of aluminum chloride.[501] Acetanilide with *tert*-butyl chloride and aluminum chloride in 1,2-dichloroethane solution gives a 94 per cent yield of *p-tert*-butylacetanilide:



In the same way, condensation was effected with acetanilide and isopropyl chloride, *sec*-butyl chloride and isoamyl chloride.

Ring compounds of nitrogen.—4-Aminoanthraquinoneacridone and α-chloroanthraquinone condense in the presence of aluminum chloride with halogen replacement to give 4-α-anthraquinonylaminoanthraquinone-1,2-acridone [502]:



Aluminum chloride may be used as catalyst in condensations with benzselenazoles. Interaction of 1-thiolbenzselenazole with 1-chlorobenzthiazole and aluminum chloride in carbon disulfide yields 1-benzthiazyl-1-benzselenazyl sulfide, claimed for use as an accelerator in the vulcanization of rubber.[503]

Compounds of Sulfur

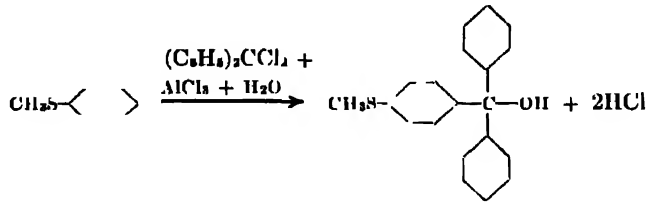
In spite of the fact that organic compounds of sulfur are easily decomposed and resinified by aluminum chloride, the catalyst has been found useful in Friedel-Crafts condensations with sulfur chloride.* In some

[500] Russ. P. 51,908 (1937) to N. S. Drozdov; *C. A.*, 34, 1334.
[501] U. S. P. 2,092,970 (1937), *C. A.*, 31, 7894; U. S. P. 2,092,972 (1937), *C. A.*, 31, 7888; U. S. P. 2,092,973 (1937), *C. A.*, 31, 7893; all to B Horstein (to U. S. Industrial Alcohol Co.); British P. 466,550 (1936), *Brit. Chem. Abs.*-B, 760 (1937); French P. 811,852 (1937), *C. A.*, 32, 593; both to U. S. Industrial Alcohol Co.
[502] German P. 262,252 (to Farbwerke vorm Meister, Lucius and Brüning); *J. Chem. Soc. Abs.*, (1), 1073 (1913).
[503] British P. 494,602 (1938) to Wingfoot Corp.; *Brit. Chem. Abstracts*-B, 81 (1939).

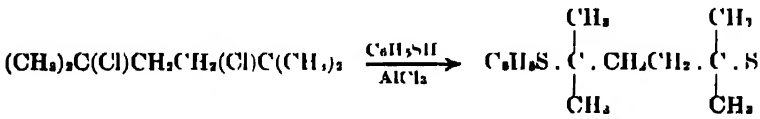
* See page 163.

cases it has catalyzed the smooth condensation of thio- compounds with acid halides.† In Friedel-Crafts alkylations, however, it has been of little value. Resinification usually occurs before condensation can be effected; if the expected reaction product is formed it is only in very small amounts.

Normal Friedel-Crafts condensation has been shown to occur with a thiophenol ether and diphenyldichloromethane. By the action of 10 g of aluminum chloride upon 12 g of the halide and 6.5 g of phenyl methyl sulfide in 100 cc of carbon disulfide there results *p*-(methylmercapto)triphenyl carbinol (m.p. 67°) according to the scheme [504]:



2,5-Dichloro-2,5-dimethylhexane condenses with thiophenols to give diaryl dithio ethers, the reaction with thiophenol proceeding thus:

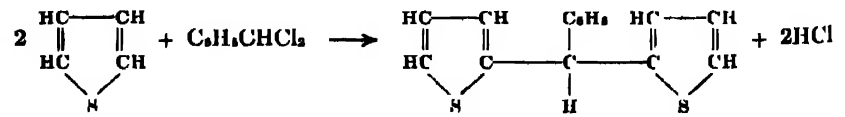


The thiocresols react analogously.[505]

Friedel-Crafts condensation of thiophene with alkyl halides may be effected, but in very low yields. In 1886, Schleicher [506] was able to isolate a small amount of isopropylthiophene, an oil b. 153-154°, by adding aluminum chloride in small portions to a mixture of thiophene and isopropyl bromide dissolved in light petroleum. Much resinification occurred during the reaction.

The use of tin tetrachloride, a milder catalyst, permits condensation of benzyl chloride with thiophene, with formation of little resinous material. Diphenylthienylmethane, m. 65°, and dibenzohydrylthiophene are secured as reaction products, the latter in 50 per cent yield.[507]

The action of benzal chloride on thiophene in the presence of aluminum chloride gives a small yield of phenyl-di-α-thienylmethane [508]:

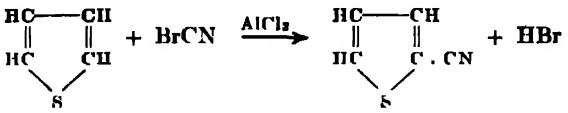


† See page 375.

[504] K. Brand and W. Vogt, *J. prakt. Chem.*, 107, 383-390 (1924); *C. A.*, 18, 2513
[505] H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, 62, 38-44 (1940)
[506] E. Schleicher, *Ber.*, 19, 672-674 (1886); *J. Chem. Soc. Abs.*, 534 (1886)
[507] G. Stadnikov and I. Goldfarb, *Ber.*, 61, 2341-2342 (1928); *C. A.*, 23, 1409
[508] A. Tohl and A. Nahke, *Ber.*, 29, 2205-2207 (1896).

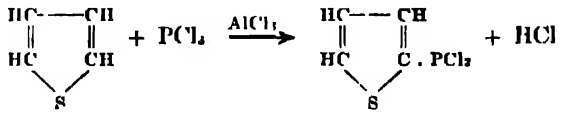
The same product is also obtained by condensation of benzotrichloride with thiophene and aluminum chloride.[509] No trithienylphenylmethane is formed in the reaction.

The preparation of nitriles by condensation of aromatic hydrocarbons with freshly prepared cyanogen bromide in the presence of aluminum chloride has been extended to thiophene.[510] An excellent yield of thiophene nitrile was secured. The condensation probably occurred with substitution at the 2-position:



The reaction has also been shown to yield a small amount of bromothiophene.[511]

Aromatic hydrocarbons condense smoothly with phosphorus trichloride in the presence of aluminum chloride to give arylchlorophosphines.[512] An attempt has been made to apply the reaction to thiophene [513]:



Although the expected thiophene chlorophosphine was secured, the yield was so poor that the reaction is not suitable for the preparation of large amounts of the compound.

Ring Compounds of Oxygen

Although unsubstituted furan has not been reported to undergo Friedel-Crafts alkylation with alkyl halides, furan has been ascribed super-aromatic properties in that the condensation, typical of aromatic compounds, occurs with furans in which decidedly negative substituents are present.[514] It has been pointed out that substitution becomes increasingly difficult in the series: pyrrole, furan, thiophene, benzene.[515]

The relative aromaticity of furan has been studied by means of applying various unit processes to it. Nitration, bromination, and sulfonation show that furan is more aromatic than benzene, toluene, or anisole.[516]

However, amino- furans have been found to have less aromatic properties than do aromatic amines. On this basis, Stevenson and Johnson [517]

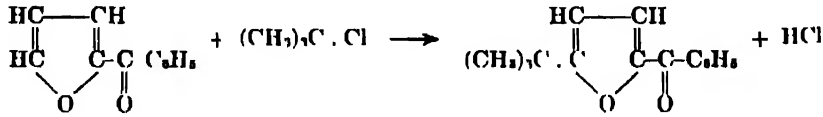
[509] A. Nahke, *Ber.*, 30, 2041-2043 (1897).
[510] P. Karrer and E. Zeller, *Helv. Chim. Acta*, 2, 482-486 (1919). *C. A.*, 14, 743. P. Karrer, A. Rebmann, and E. Zeller, *Helv. Chim. Acta*, 3, 261-272 (1920); *J. Chem. Soc. Abs.*, 118 (I), 389 (1920)
[511] W. Steinkopf, *Ann.*, 430, 80 (1923).
[512] A. Michaelis, *Ann.*, 293, 193-225 (1896); 294, 1-55 (1896).
[513] H. Sachs, *Ber.*, 25, 1514-1518 (1892).
[514] H. Gilman and N. O. Calloway, *J. Am. Chem. Soc.*, 55, 4197-4205 (1933).
[515] T. Reichstein, *Helv. Chim. Acta*, 13, 349-356 (1930); *C. Z.*, 1930, II, 399.
[516] J. M. Straley, *Iowa State College J. Sci.*, 11, 115-117 (1936).
[517] H. B. Stevenson and J. R. Johnson, *J. Am. Chem. Soc.*, 59, 2525-2532 (1937)

attribute to furan only weakly aromatic properties rather than super-aromaticity.

Aluminum chloride has been found to be an especially efficient catalyst in the alkylation of furans, the order in decreasing efficiency of several catalysts investigated being: aluminum chloride, ferric chloride, and stannic chloride.[518] Although in the alkylation of aromatics, a trace of the catalyst is generally sufficient to effect reaction, for the furans a molecular equivalent of the catalyst must be used. This is comparable to the molecular equivalent of catalyst required in Friedel-Crafts acylation of aromatics. Aluminum chloride is not an effective catalyst for acylation of furans.

In the alkylation of furan derivatives, the entering alkyl group generally takes an α-position if it is available. With di-α-substituted furans, the position taken by the entering group is dependent upon directive influences of the substituents already present. For example, if in a di-α-substituted furan one of the substituents is an *ortho, para*-director in benzene, and the other a *meta*-director, the entering group is directed to the β-position contiguous to the *ortho, para*-director.[519] Exceptions to this rule of orientation have been found to occur, however, and will be noted later.

Gilman and Calloway [514] have demonstrated the super-aromaticity of furan by alkylating furan esters, acids, ketones, and aldehydes. In the aromatic series, these reactions occur only with those compounds, *e.g.*, derivatives of phenol ethers or of polynuclear compounds, which have pronounced aromatic characteristics. With aluminum chloride as catalyst, in carbon disulfide solution, 2-furyl phenyl ketone condenses with *tert*-butyl chloride to give 5-*tert*-butyl-2-furyl phenyl ketone, in 30 per cent yield:



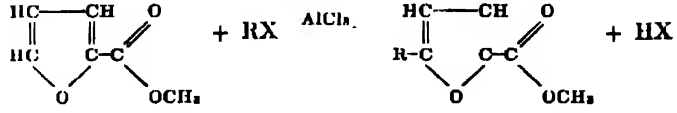
2-Furoic acid was likewise alkylated with *n*-butyl chloride in the presence of an excess of aluminum chloride to give a 6 per cent yield of 5-*tert*-butyl-2-furoic acid. Here the entering substituent also goes into the free α-position.

The same type of condensation occurs with furoic esters. Although no reaction occurs with methyl or ethyl halides, methyl 2-furoate has been condensed with other alkyl halides in the presence of aluminum chloride and carbon disulfide, with cooling, to yield the indicated products:

[518] H. Gilman and R. Burtner, *J. Am. Chem. Soc.*, **57**, 909-912 (1935).
[519] H. Gilman, N. O. Calloway, and E. W. Smith, *J. Am. Chem. Soc.*, **56**, 220-221 (1934).

Alkyl halide	Product	% Yield
n-Propyl chloride	methyl 5-isopropyl-2-furoate	48
Isopropyl chloride	methyl 5-isopropyl-2-furoate	42
n-Butyl chloride	methyl 5-*tert*-butyl-2-furoate	45
Isobutyl bromide	methyl 5-*tert*-butyl-2-furoate	66
sec-Butyl bromide	methyl 5-*tert*-butyl-2-furoate	1.6
tert-Butyl bromide	methyl 5-*tert*-butyl-2-furoate	46
n-Amyl chloride	methyl 5-amyl-2-furoate	31
n-Hexyl bromide	methyl 5-hexyl-2-furoate	57.1

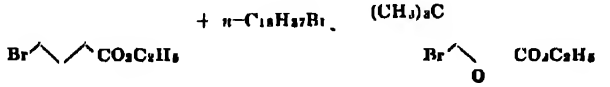
Here the entering substituent also takes the free α-position:



The condensation of *tert*-amyl halide with ethyl 2-furoate likewise gives the 5-alkyl derivative, ethyl 5-*tert*-amyl-2-furoate, in the presence of aluminum chloride in carbon disulfide solution. In like manner, ethyl 5-(1-methylcyclohexyl)-2-furoate is obtained.[520]

In the alkylation of brominated ethyl furoates with higher alkyl halides, it was noted that the higher alkyl groups are cleaved and rearranged during the reaction.[521] Thus, alkylation of ethyl 5-bromo-2-furoate with *n*-, iso-, and *tert*-butyl halides gives the same product, ethyl 4-*tert*-butyl-5-bromo-2-furoate. Unexpectedly, the product of the alkylation of ethyl 5-bromo-2-furoate with *n*-amyl chloride, *n*-hexyl bromide, and *n*-octadecyl bromide is also ethyl 4-*tert*-butyl-5-bromo-2-furoate.

Cleavage-rearrangements in Friedel-Crafts alkylations were further investigated.[522] Preceding work was substantiated by the fact that ethyl 5-bromo-2-furoate with *n*-octadecyl bromide and aluminum chloride was found to give a 46 per cent yield of ethyl 4-*tert*-butyl-5-bromo-2-furoate:



Another unusual phenomenon was observed in the alkylation of ethyl 5-bromo-2-furoate with *n*-amyl bromide. Here cleavage and rearrangement took place, but there was also replacement of the furan bromine, so that substitution occurred in the 5-position. Ethyl 5-*tert*-butyl-2-furoate was thus obtained in 31-40 per cent yields. By varying reaction conditions it was found possible to obtain either a mixture of ethyl 5-*tert*-butyl-2-furoate with ethyl 4-*tert*-butyl-5-bromo-2-furoate, or the latter compound exclusively. Bromine-replacement was traced to the influence of the ferric chloride content of the aluminum chloride used.

In the alkylation of ethyl 4-bromofuroate with *n*-amyl chloride the

[520] T. Reichstein, H. R. Rosenberg, and R. Eberhardt, *Helv. Chim. Acta*, **18**, 721-724 (1935); *C. A.*, **29**, 6232.
[521] H. Gilman and R. Burtner, *J. Am. Chem. Soc.*, **57**, 909-912 (1935).
[522] H. Gilman and J. A. V. Turek, *J. Am. Chem. Soc.*, **61**, 473-478 (1939).

bromine atom was removed, but it was not replaced. The product was ethyl 5-*tert*-butyl-2-furoate. Cleavage of the amyl group had occurred. Since ethyl 2-furoate alkylates without cleavage, the bromine atom must have been removed after the alkylation and not before.

In order to clarify the mechanism underlying cleavage in Friedel-Crafts alkylations of furans, ethyl 5-bromo-2-furoate was alkylated with a number of higher alkyl halides. In every case ethyl 4-*tert*-butyl-5-bromo-2-furoate was obtained, the yields varying with the alkyl halide used:

Alkyl halide used	% yield of ethyl 4-*tert*-butyl-5-bromo-2-furoate
n-C_4H_9Cl	26
t-C_4H_9Br	15
n-$C_5H_{11}Cl$	15
t-$C_5H_{11}Cl$	6
i-$C_5H_{11}Br$	20
n-$C_5H_{11}I$	25
n-$C_6H_{13}Cl$	20
n-$C_6H_{13}Br$	6
n-$C_{12}H_{25}Br$	13
n-$C_{16}H_{33}Br$	20
n-$C_{18}H_{37}Br$	46

It was concluded that the *tert*-butyl radicals did not come from the furan ring itself and that the 4-carbon radical was the result of cleavage of the alkyl halide probably during, or simultaneously with, the alkylation.

In the Friedel-Crafts reaction of 2-furfural with isopropyl chloride, the identity of the product could not be established at first.[518] Later,[521] it was ascertained that the alkylation had taken an anomalous course, the reaction product being 4-isopropyl-2-furfural. Here, in spite of the fact that a free α-position was available, the entering alkyl group had gone into a β-position.

This was all the more contradictory because, in alkylation of 2-furfural with butyl or amyl chlorides, the alkyl group was later introduced into the 5-position. In the alkylation of 2-furfural with these higher alkyl chlorides, however, the predominating product isolated is the one in which the alkyl group is most highly branched. That is, *n*-, iso-, and *tert*-butyl chlorides all give 5-*tert*-butyl-2-furfural. During alkylation of 2-furfural, the aluminum chloride doubtless has an isomerizing effect In the reaction with isopropyl chloride, the alkyl group may have first gone to the 5-position, and was then subsequently rearranged to the 4-position. This supposition, however, was not borne out when 5-isopropyl-2-furfural was treated with aluminum chloride; here no rearrangement was noted.[524]

Little is known concerning condensations of polynuclear ring compounds of oxygen with alkyl halides and aluminum chloride. It has been claimed, however, that diphenylene oxide may be condensed with chlor-

[518] H. Gilman, M. McCorkle, and N. O. Calloway, *J. Am. Chem. Soc.*, **56**, 745 (1934). H. Gilman N. O. Calloway, and R. R. Burtner, *Ibid.*, **57**, 906-907 (1935)
[521] H. Gilman and R. R. Burtner, *J. Am. Chem. Soc.*, **57**, 909-912 (1935).

nated paraffin in the presence of aluminum chloride to give a viscous oil, which reduces the congealing point of lubricating oil.[525]

Diphenylene oxide reacts with 2,5-dichloro-2,5-dimethylhexane and aluminum chloride, with the introduction of a new hydroaromatic cycle or cycles into the aromatic nucleus.[526]

[525] German P. 626,602 (1936) to F. Hofmann and E. Dietzel (to Oberschlesischer Berg und Hüttenmännischer Verein); *C. A.*, **30**, 5782.

[526] H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, **62**, 38-44 (1940); see p. 432 for analogous reaction with phenols.

Chapter 6

Friedel-Crafts Syntheses. Part 2. Ketone Syntheses

Scope of the Reaction

Acyl halides react with aromatic hydrocarbons in the presence of aluminum chloride to yield ketones:

$$RH + R'COCl \xrightarrow{AlCl_3} \begin{matrix} R \\ \diagdown \\ C{=}O \\ \diagup \\ R' \end{matrix} + HCl$$

The reaction is general for mono- and polynuclear hydrocarbons and for halogenated hydrocarbons, phenols, and phenol ethers. Electronegative groups, when substituted in the hydrocarbon component, have an inhibiting effect on the reaction. This retarding tendency is especially evidenced with benzene and mono-alkylated benzenes, substitution of the acyl group in the nucleus of benzophenone, benzoic acid, or nitrobenzene being completely prevented. It is not so pronounced with negatively substituted polyalkylated benzenes, phenols, or phenol ethers. Here the presence of the activating alkyl, hydroxy-, or alkoxy- groups may diminish the inhibiting tendency of the negative groups to such an extent that Friedel-Crafts acylation takes place. The presence of negative groups in polynuclear hydrocarbons also does not have as inhibiting an effect as in benzene, the high aromaticity of the polynuclear reactant in itself often having a sufficiently activating effect to permit substitution. To an even greater extent this is also true for such highly active heterocyclic compounds as thiophene and furan; although phenyl benzoate resists acylation, furan esters readily undergo the reaction.

Substituents in the acyl halide component do not have so great an effect; thus, although *o*- or *m*-nitrobenzophenones cannot be prepared by reaction of nitrobenzene with benzoyl chloride, they can be prepared by condensation of *o*- or *m*-nitrobenzoyl chloride with benzene. It has been shown, however, that the presence of negative groups in the acyl halide has a retarding influence, but that it is not so pronounced as the presence of negative radicals in the aromatic compound which is to be substituted [1]

The order of reactivity for acyl halides in the Friedel-Crafts ketone synthesis has been found by Calloway [2] to be acyl iodide > acyl bromide

[1] S. C. J. Olivier, *Rec. trav. chim.*, 33, 244-261 (1914); *C. A.*, 9, 442.
[2] N. O. Calloway, *J. Am Chem. Soc.*, 59, 1474-1478 (1937)

> acyl chloride > acyl fluoride. This is just opposite to the order determined for alkyl halides in Friedel-Crafts alkylations.

Since the reactivity of both the aromatic compound to be substituted and the acyl halide is a factor in ease of reaction, generalities concerning the scope of Friedel-Crafts ketone syntheses are difficult to formulate. The synthesis is more or less applicable to the whole field of organic chemistry. Originally considered to be limited to the aromatic series, it has been extended to the acylation of aliphatic compounds.*

Theoretical Discussion

Essentially, the ketone synthesis differs from Friedel-Crafts alkylations in that it requires at least a molecular quantity of aluminum chloride with respect to the acyl halide, whereas alkylation requires only catalytic amounts. This is probably due to the fact that acyl halides form comparatively stable molecular complexes with aluminum chloride, thereby diminishing its catalytic effect. A discussion of the role of complexes in Friedel-Crafts ketone synthesis and a resume of physico-chemical studies of the reaction is given here. An interpretation of this work in the light of electronic concepts is also found in the more general chapter on mechanism of reactions catalyzed by aluminum chloride.†

The mechanism of Friedel-Crafts ketone synthesis has been studied more extensively than that of other Friedel-Crafts reactions. This is probably due to the fact that aluminum chloride forms well-characterized complexes with acid chlorides and with the ketones produced. Although it has not been definitely shown that complex formation is a primary requisite of all Friedel-Crafts reactions, early investigators took advantage of the well-defined addition products formed as a means of tracing the mechanism involved.

According to Gustavson,[3] acyl halides, when acted on by aluminum chloride, evolve hydrogen chloride; an unsaturated radical containing oxygen is produced, and remains combined with the aluminum chloride,

$$Al_2Cl_6 + 4C_6H_5OCl \longrightarrow Al_2Cl_6.C_{28}H_{20}O_4 + 4HCl$$

Kronberg [4] regarded the constitution of the additive compound of benzoyl chloride with aluminum chloride to be $C_6H_5CCl_2.O.AlCl_2$. According to him, this reacts with benzene to form the additive compound of benzophenone and aluminum chloride which he formulated as $C(C_6H_5)_2Cl.O.AlCl_2$. The latter was said to be decomposed by water into benzophenone and aluminum oxychloride.

The majority of the investigators, however, believe that the additive compounds of aluminum chloride have the composition $RCOCl.AlCl_3$. Böeseken [5] reports that acetyl chloride combines with aluminum chloride in carbon disulfide solution at $-10°$, giving the additive compound

* See Chapter 17.
† See Chapter 4.
[3] G. Gustavson, *Bull. soc. chim.* (2), 42, 325-327 (1884); *cf. J. prakt. Chem.* (2), 37, 106-110 (1888).
[4] H. Kronberg, *J. prakt. Chem.* (2), 61, 494-496 (1900); *J. Chem. Soc. Abs.*, 78 (I), 802 (1900).
[5] J. Böeseken, *Rec. trav. chim.*, 20, 102-106 (1901); *J. Chem. Soc. Abs.*, 80 (I), 474 (1901).

$CH_3COCl.AlCl_3$. It is a non-crystallizable, yellow syrup which interacts with benzene in carbon disulfide solution to form the compound $COC_6H_5.CH_3.AlCl_3$, melting at 64°. This, when decomposed by water, yields acetophenone.

Well-defined crystalline compounds of aluminum chloride with acyl chlorides having the compostion $RCOCl.AlCl_3$ have been reported and investigated by Menshutkin,[6] Perrier,[7] Böeseken,[8] and Olivier.[9]

Perrier [7] attempted to explain the function of aluminum chloride in this reaction by assuming that the formation of ketones takes place in two stages:

(1) $2RCOCl + Al_2Cl_6 \longrightarrow (RCOCl)_2,Al_2Cl_6$

(2) $(RCOCl)_2,Al_2Cl_6 + C_nH_n \longrightarrow 2HCl + (RCO.C_nH_{n-1})_2,Al_2Cl_6$

He considered that the synthesis proceeded best when the additive compound of acid chloride and aluminum chloride was prepared first, and the hydrocarbon caused to react with the complex thus obtained.

Perrier and Caille [10] have worked out a process for the separation of isomeric naphthyl ketones obtained by Friedel-Crafts reaction which depends upon the difference in stability and solubility in carbon disulfide of their aluminum chloride addition products.

Böeseken [8] postulates a similar scheme, and assumes that the reaction proceeds in three stages:

(1) $RCOCl + AlCl_3 \longrightarrow RCOCl,AlCl_3$

(2) $RCOCl,AlCl_3 + HR' \longrightarrow RCOR',AlCl_3 + HCl$

(3) $RCOR',AlCl_3 + nH_2O \longrightarrow RCOR' + AlCl_3,nH_2O$

Here HR' represents an aromatic hydrocarbon or one of its derivatives, *e.g.*, alkylated aromatics or ethers.

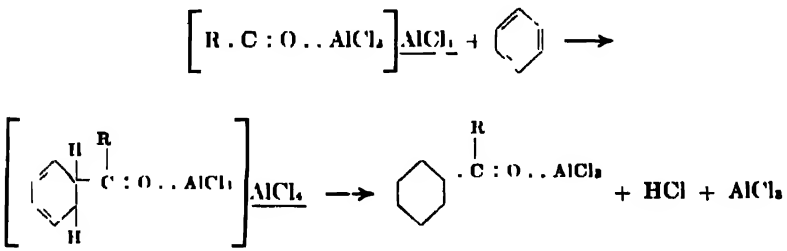
In the condensation of acyl chlorides with aromatic hydrocarbons or their derivatives, *para*-substituted ketones are almost invariably produced. This appears to be caused by the directive influence of the aluminum chloride, which Böeseken [11] suggests is unable to form compounds of the type $R.CO(AlCl_3).C_6H_4X$, where the substituent X is in the ortho-position to the carbonyl.

The existence of aluminum chloride complexes with acetophenone and with benzophenone has been confirmed by Menshutkin.[12] The complex with acetophenone, $C_6H_5COCH_3.AlCl_3$, crystallized slowly and easily became resinous; it was, therefore, investigated only qualitatively. On the other hand, the complex $C_6H_5COC_6H_5.AlCl_3$ appeared to be a definite compound, crystallizing in very long yellow needles which melted at 130°. In summarizing his studies on binary mixtures of

[6] B. N. Menshutkin, *J. Russ. Phys.-Chem. Soc.*, 42, 1310-1318 (1910); *C. A.*, 6, 735.
[7] G. Perrier, *Ber.*, 33, 815-816 (1900); *J. Chem. Soc. Abs.*, 78 (I), 33 (1900)
[8] J. Böeseken, *Rec. trav. chim.*, 19, 19-26 (1900); *J. Chem. Soc. Abs.*, 78 (I), 349 (1900).
[9] S. C. J. Olivier, *Rec. trav. chim.*, 54, 943-944 (1935); *C. A.*, 30, 2084
[10] G. Perrier and H. Caille, *Compt. rend.*, 146, 769-770 (1908); *C. Z.*, 1908, I, 1928.
[11] J. Böeseken, *Rec. trav. chim.*, 23, 98-109 (1904); *J. Chem. Soc. Abs.*, 86 (I), 384 (1904).
[12] B. N. Menshutkin, *Iswestja Peterburger Polytech.*, 13, 1-16; *J. Russ. Phys.-Chem. Soc.*, 42, 1298-1308 (1910); *C. Z.*, 1910, II, 154-155.

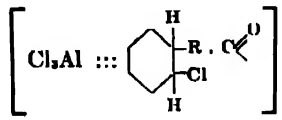
aluminum chloride, Menshutkin [13] points out that since complexes of aluminum chloride are so often readily characterized by thermal studies, this method affords an effective means of studying the kinetics of Friedel-Crafts reactions. From studies dealing with use of antimony tribromide or trichloride as catalyst he concluded [14] that the first phase of the reaction between an aromatic hydrocarbon and an acyl halide in the presence of a metal halide is the formation of a complex of the hydrocarbon and the catalyst, and that the second phase of the reaction consists in the action of the acyl chloride on this compound, with liberation of hydrogen chloride and the formation of ketone in combination with the catalyst.

Dilthey[15] draws a parallel between the acetoacetic ester synthesis and the Friedel-Crafts synthesis, advancing the following scheme for Friedel-Crafts ketone synthesis:



Here only the underlined molecule of aluminum chloride has a catalytic effect. According to this scheme, the use of more than one molecule of aluminum chloride is indicated; the first molecule is tied up in the R.C:O.$AlCl_3$ complex; a slight excess, however, catalyzes condensation. If Dilthey's explanation is correct, then the use of 90 to 95 per cent aluminum chloride would give no reaction. As a matter of fact, the degree of ketone formation is practically proportional to the aluminum chloride content.[16]

Previously, Schaarschmidt [17] had also postulated a complex in which the formation of a dihydrobenzene was assumed.



Secondary reactions occur between this product and the metallic chloride, so that stoichiometric amounts of aluminum chloride are required for reaction to occur.

[13] B. N. Menshutkin, *Ann. Inst. Analyse physico-chim.*, 2, 61-95 (1922) *C. A.*, 18, 1651.
[14] B. N. Menshutkin, *J. Russ. Phys.-Chem. Soc.*, 46, 259-283 (1914); *J. Chem. Soc. Abs.*, 106 (I), 873 (1914).
[15] W. Dilthey, *Ber.*, 71, 1350-1358 (1938).
[16] P. H. Groggins, *Personal communication.*
[17] A Schaarschmidt, *Z. angew. Chem.*, 37, 286-288 (1924); *C. A.*, 18, 2874.

According to Prins,[18] dihydrobenzene resinifies upon treatment with aluminum chloride; hence it cannot be an intermediary in Friedel-Crafts reactions. Prins believes that under the influence of aluminum chloride benzene acts as if it had a mobile hydrogen atom, and compares the C-H group in benzene to an O-H group in alcohols.

Physico-chemical studies.—Steele [19] made a dynamic study of the Friedel-Crafts ketone synthesis. He concluded that the reaction is unimolecular when less than one mole of catalyst is used, if the hydrocarbon is in large excess. However, in the presence of an excess of the condensing agent, the reaction, instead of being unimolecular, becomes bimolecular, and is best explained by assuming that the reagents are two intermediate compounds, each containing aluminum chloride. Steele followed the course of the reaction by passing a rapid current of hydrogen through the reaction mixture and titrating the hydrogen chloride thus carried over. He plotted a curve for the desaturation of a saturated solution of hydrogen chloride in the aromatic hydrocarbon, and corrected his titrations by adding the amounts remaining dissolved at corresponding times as read from this curve He [20] reached the following conclusions:

1. The mechanism suggested by Perrier and Böeseken is well established, provided the ratio of aluminum chloride to acid chloride is not greater than unity. The reaction is unimolecular
2. In the presence of an excess of aluminum chloride, the reaction is best explained as being bimolecular, the reacting species being two intermediate compounds, each containing aluminum chloride.
3. The action ceases at a point when all the metallic chloride is withdrawn from the system as a component of the final product

Olivier [21] advanced the same theories concerning the mechanism of the reaction, *i.e.*, that the acyl chloride first forms an additive compound with the catalyst. He studied the velocity of the reaction by taking samples of the reaction mixture at different time intervals and determining the unreacted benzoyl chloride. The results of the experiments show that the reaction is monomolecular, and that the yield is based on the quantity of the minor component. The data for different concentrations of aluminum chloride (0.1 and 0.2 mole) show that $K_{0.2}/K_{0.1} = \pm 1.30$. The method of measuring the progress of the reaction was as follows: an accurately measured sample was pipetted off and dropped into excess dilute caustic. Hydrolysis was completed by boiling for one hour under reflux. After acidification, the benzene was removed by heating. The solution was then extracted with ether and each extract washed carefully with water. The wash water was returned and extraction continued. The ether layers were united, evaporated, dissolved in 95 per cent alcohol and the benzoic acid titrated, using phenolphthalein as indicator. The titer is the measure of the unreacted benzoyl chloride. The use of an excess of benzoyl chloride in the reaction was found to be without material

[18] H. J. Prins, *Chem. Weekblad.*, 24, 615-619 (1927); *C. A.*, 22, 716.
[19] B. D. Steele, *Proc. Chem. Soc.*, 19, 209-210 (1903).
[20] B. D. Steele, *J. Chem. Soc.*, 83, 1470-1490 (1903).
[21] S. C. J. Olivier, *Rec. trav. chim.*, 37, 305-340 (1918); *J. Chem. Soc. Abs.*, 114, 228 (1918).

influence on the velocity of the reaction or yield of the ketone Olivier found the reaction constant of the reaction

$$C_6H_5COCl.AlCl_3 + C_6H_6 \longrightarrow C_6H_5COC_6H_5.AlCl_3 + HCl$$

to be in good agreement.

Martin and co-workers [22] found Steele's method to be more rapid and convenient than that used by Olivier, in whose study of the reaction benzene with benzoyl chloride the benzoyl chloride had to be hydrolyzed and the benzoic acid extracted with ether for titration. Martin and co-workers found that the removal of the acid from the solution was much slower than Steele had supposed it to be and they recalculated his data They investigated mixed catalysts covering a wide range of composition of aluminum chloride and ferric chloride. At comparable concentrations the activity increases with increasing mole percentage of ferric chloride and reaches a maximum at percentages in excess of 50 mole per cent The mixed catalysts have been shown to produce less than one mole of product for each mole of total metal chlorides present. It is shown that the catalyst is removed in the form of a bimetal complex with the reaction product, such as $C_6H_5COC_6H_4CH_3.AlCl_3.FeCl_3$. In an $AlCl_3.FeCl_3$ catalyst containing 16 4 mole per cent of ferric chloride, the ratio $HCl/AlCl_3$ is very nearly unity, which agrees with the mechanism that the ferric chloride is combined as $C_6H_5COC_6H_4CH_3.AlCl_3.FeCl_3$, while the remaining aluminum chloride is removed as $C_6H_5COC_6H_4CH_3.AlCl_3$.

Martin and co-workers have found that the reaction velocity increases markedly with increase of the concentration of the reacting substances. At comparable concentrations, there is a large increase in activity of the mixed catalyst as ferric chloride is added. Gulf Refining Company aluminum chloride was much more active than could be accounted for by its ferric chloride content alone; its greater activity was thought to be due partly to the titanium chloride which it contains.

Kinetic investigations of Friedel-Crafts ketone have been made by Ulich and Heyne.[23] The courses of the reactions were followed by measuring volumetrically the hydrogen chloride evolved. When equivalent amounts of aluminum chloride and benzoyl chloride are used, the rate follows the unimolecular rule. The reaction was found to be retarded as it goes on by formation of a complex between aluminum chloride and the benzophenone formed. This complex is obviously more stable than the $AlCl_3.C_6H_5COCl$ complex postulated as intermediate.

Olivier [24] believed that the failure of Ulich and Heyne to obtain consistent results was due either to failure to keep conditions precisely fixed, or to the use of less accurate methods for following the reaction.

Subsequently, Ulich and Fragstein [25] followed the rate of reaction of

[22] L. F. Martin, P. Pissolato, and L S. McWaters, *J. Am. Chem. Soc.*, 57, 2584-2589 (1935), *C. A.*, 30, 1750.
[23] H Ulich and G. Heyne, *Z. Elektrochem.*, 41, 509-514 (1935); *C. A.*, 29, 7768.
[24] S. C. J. Olivier, *Rec. trav. chim.*, 54, 943-944 (1935); *C. A.*, 30, 2084.
[25] H. Ulich and F. v. Fragstein, *Ber.*, 72, 630-636 (1939).

benzene with $C_6H_5COCl.AlCl_3$ at 30°. The hydrogen chloride evolved was measured volumetrically, and the total chlorine and unreacted benzoyl chloride in the liquid was analyzed. Results were in fair agreement with those of Olivier,[24] although the increase of the first order constant with benzoyl chloride concentration appears less than that reported by Olivier. Ulich and Fragstein found the average velocity constant to be 0.00172. The concentration had a certain influence on the velocity constant: the average of 4 measurements with less than 0.25 mole of the complex per liter was 0.00156, and that of 5 measurements with more than 0.25 mole per liter was 0.00183. The constants found by Olivier increased from 0.0023 to 0.00355 in the range of 0.1 to 0.3 mole per liter.

It has been shown experimentally [26] by the use of radioactive aluminum chloride, that an interchange of chlorine atoms takes place between acetyl chloride and aluminum chloride:

$$CH_3COCl + AlCl \longrightarrow (CH_3CO)^+ + (AlCl_4)^-$$

in the absence of any third reactant or evolution of hydrogen chloride. It was therefore concluded that the first stage in the ketone synthesis was the "ionization," under the influence of aluminum chloride, of the covalent C—Cl bond, with the formation of the ion $(AlCl_4)$ and a positive carbonium ion.

In this connection it is of interest that recently Norris and Klemka[27] have shown that an interchange of halogen occurs in the reaction of acetyl bromide with benzene in presence of aluminum chloride. Here the hydrogen halide evolved was not pure hydrogen bromide; instead, 70 per cent of it was hydrogen chloride. Conversely, the reaction of acetyl chloride and benzene in presence of aluminum bromide resulted in the evolution of 77 mole per cent of hydrogen bromide.

Dipole moments and molecular weights of aluminum chloride complexes with benzoyl chloride and benzophenone have been measured. Data indicate a tetrahedral configuration with the aluminum atom as a center.[28]

Effect of solvents.—The influence of different solvents on the reaction of benzene with acetyl chloride and aluminum chloride has been studied [29] by titrating the hydrogen chloride liberated. The speed of the reaction was found to depend on the density and volume of the solvent employed. The following conclusions were reached:

Benzene: Maximum speed; addition of aluminum chloride to the precipitated mixture caused formation of a soluble complex.
Ligroin: The speed of reaction was nearly equal to that in benzene but there was appreciable falling off after the initial evolution of hydrogen chloride; the complex formed is insoluble.
Chloro- or bromobenzene: At the start the reaction is fairly rapid

[26] F. Fairbrother, *J. Chem. Soc.*, 503-506 (1937).
[27] J. F. Norris and A. J. Klemka, *J. Am. Chem. Soc.*, 62, 1428-1432 (1940).
[28] H. Ulich and W. Nespital, *Z. Elektrochem.*, 37, 559-563 (1931); 44, 750-753 (1931).
[29] M. Chopin, *Bull. soc. chim.*, 35, 610-614 (1924); *C.* 1, 18, 2558-9.

Carbon disulfide: The reaction is slower than the above solvents, but it is more regular.
Nitrobenzene: When aluminum chloride is in suspension, the speed of the reaction is rapid, declining as the catalyst goes into solution.

Calloway and Green [30] studied the effect of solvents on side reactions. It was found that in the reaction of benzene and acetyl chloride, with aluminum chloride in carbon disulfide, the evolution of hydrogen chloride never ceases. The evolution of hydrogen chloride is, therefore, not a satisfactory criterion for judging the reaction conditions. The use of an insufficient proportion of aluminum chloride tends to encourage condensation of the ketones primarily formed. Some dypnone, $C_6H_5\overset{CH_3}{\overset{|}{C}}{:}CHCOC_6H_5$, is formed if the ratio of acetophenone to aluminum chloride is greater than 1:1. When 2 moles of acetophenone and 1 mole of aluminum chloride in carbon disulfide are present, 73 per cent of dypnone is formed at 40-50°. Therefore, the formation of β-unsaturated ketones is one of the side reactions to be considered in the preparation of ketones.

As has been pointed out elsewhere in this book,* ease of reaction is the determining factor in the choice of solvent for all reactions catalyzed by aluminum chloride. As the reactivity of the compound to be substituted is increased, better results are secured if a solvent is used which ties up some of the catalyst by forming a complex with it. Nitrobenzene and *sym*-tetrachloroethane are the solvents generally used in condensations of phenols, polynuclear hydrocarbons, or active heterocyclic compounds with acyl halides in presence of aluminum chloride. With less reactive constituents, an excess of the compound which is to be substituted is used. In some cases, especially when the hydrocarbon used is a solid, an excess of the acyl halide has given good results. Carbon disulfide is a useful solvent for reactions effected with slowly reacting nonliquid components. In acylation of benzene, even with such reactive acyl halides as *p*-methoxybenzoyl chloride, better yields are obtained if excess of benzene, rather than carbon disulfide, is used as diluent.[31]

Reaction of Benzene with Simple Aliphatic Acid Chlorides

There are several procedures which may be used for the reaction of benzene with simple acyl halides. Generally, the hydrocarbon and acyl chloride, with or without a solvent, are gradually treated with aluminum chloride, and the whole warmed on a water-bath until the evolution of hydrogen chloride ceases.[32] Perrier's [33] modification of the reaction may be used, in which case the acyl chloride is reacted with aluminum chloride in carbon disulfide solution and then caused to react with the hydro-

[30] N. O. Calloway and L. D. Green, *J. Am. Chem. Soc.*, **59**, 809-811 (1937).
* See Chapter 21.
[31] P. J. Montagne, *Rec. trav. chim.*, **40**, 247-248 (1921); *C. A.*, **15**, 3176.
[32] K. Elbs, *J. prakt. Chem. (2)*, **33**, 180-188 (1886); *J. Chem. Soc. Abs.*, **50**, 461 (1886). C. Friedel and J. M. Crafts, *Ann. chim. (6)*, **1**, 507 (1884).
[33] G. Perrier, *Ber.*, **33**, 815-816 (1900); *J. Chem. Soc. Abs.*, **78** (I), 331 (1900).

carbon.[34] Or, the acyl chloride may be added to a mixture of benzene and aluminum chloride.[35]

Attempts have been made to increase yields by varying procedure. Thus, an 89 per cent yield of butyrophenone has been secured from butyryl chloride and benzene by using Perrier's modification.[36]

Use of excess aluminum chloride may increase yields. Thus, to the product obtained by adding a mixture of 150 g of propionyl chloride and 180 g of benzene to a suspension of 150 g of aluminum chloride in carbon bisulfide, there is added further aluminum chloride (about 30 g) until the evolution of hydrogen chloride has completely ceased. In this way the yield of propiophenone was increased from 50 to 88.5 per cent.[37]

The use of the indicated acid chlorides and benzene has been found to result in the production of the following ketones:

Table 7

Acid chloride	Ketone	Ref.
Butyryl chloride	butyrophenone	1
n-Valeryl chloride	valerophenone	2
iso-Valeryl chloride	*iso*-valerophenone	3, 4
n-Caproyl chloride	*n*-amyl phenyl ketone	4
Oenanthyl chloride	*n*-hexyl phenyl ketone	5, 6
Caprylyl chloride	*n*-heptyl phenyl ketone	7, 8
Lauroyl chloride	laurophenone	9
Stearoyl chloride	stearophenone	10, 11, 12

1. E. Burcker, *Ann. chim. phys. (6)*, 26, 467 (1882).
2. E. Layraud, *Bull. soc. chim. (3)*, 35, 224 (1906).
3. A. Claus, *J. prakt. chem. (2)*, 46, 489 (1892).
4. G. Schroeter, *Ber.*, 40, 1589-1604 (1907).
5. V. Auger, *Bull. soc. chim. (2)*, 47, 42-51 (1887).
6. F. Krafft, *Ber.*, 19, 2982-87 (1886).
7. V. Meyer and W. Scharwin, *Ber.*, 30, 1941-1943 (1897).
8. W. C. Hartung and others, *J. Am. Chem. Soc.*, 52, 3317-3321 (1930)
9. S. Kipping and O. F. Russell, *J. Chem. Soc.*, 67, 502-508 (1895).
10. L. A. Mikeska and others, *J. Org. Chem.*, 2, 499-505 (1938).
11. A. Claus and H. Hafelin, *J. prakt. Chem. (2)*, 54, 399 (1896).
12. F. Seidel and O. Engelfried, *Ber.*, 69, 2567-2591 (1936).

Recently, interest has arisen in industrial use of ketones prepared from higher aliphatic acid chlorides. In a patent to I. G. Farbenindustrie,[38] fatty acid halides containing at least six carbon atoms are condensed with aromatic hydrocarbons. The resulting ketones are subsequently hydrogenated for the formation of the corresponding hydrocarbons. The products are sulfonated to form wetting agents and detergents. Such use of higher fatty acid chlorides makes available the numerous higher fatty acids for use in the production of new synthetic detergents. The production of sodium dodecylbenzene sulfonate via laurophenone is thus claimed.

Unsaturated Aliphatic Monocarboxylic Acid Chlorides

Unsaturated aliphatic acid chlorides may react abnormally with benzene and its homologs, with formation of hydrindones instead of unsaturated ketones.

[34] J. Böeseken, *Rec. trav. chim.*, 20, 102-106 (1901); *J. Chem. Soc. Abs.*, 80 (1), 474 1901).
[35] L. Bouveault, *Bull. soc. chim. (3)*, 17, 1014-1021 (1897).
[36] R. Borge, *Ber.*, 35, 1085-1090 (1902).
[37] G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303-309 (1935).
[38] British P. 453,778 (1936) to W. W. Groves (to I. G. Farbenindustrie). Same as French P. 801,499; *C. A.*, 31, 1122.

By the action of acrylyl chloride on benzene in the presence of aluminum chloride, Moureu [39] obtained a small quantity of a colorless substance which he reported to be phenyl vinyl ketone. Moureu's work was repeated by Kohler,[40] who found that the supposed phenyl vinyl ketone was really 1-hydrindone. This is doubtless formed from phenyl vinyl ketone, since the latter is easily changed into 1-hydrindone upon treatment with aluminum chloride.

β,β-dimethylacrylyl chloride has been reported to condense with benzene and aluminum chloride to give isobutenyl phenyl ketone (b.p. 134-136°/12 mm) in 40 per cent yield.[41] However, previously [42] it had been reported that condensation of β,β-dimethylacrylyl chloride with benzene and aluminum chloride yields 3,3-dimethyl-1-hydrindone. Pseudocumene and the chloride yield isopropylidene-2,4,5-trimethylacetophenone.[43]

Kohler [40] reports the formation of phenyl propenyl ketone from crotonyl chloride, benzene, and aluminum chloride. Benzene, toluene, and the three xylenes were reacted with crotonyl chloride by von Auwers and Risse [44] in their study of the influence of benzene substituents on ring closure of unsaturated ketones. A hydrindone was formed only with *p*-xylene. Their results are summarized:

Hydrocarbon	Reaction Product	b.p. (°C.)
Benzene	crotonylbenzene	124-128/14 mm
Toluene	4'-methylchalcone	132-134/11 mm
o-Xylene	1,2-dimethyl-5-crotonylbenzene	138-140/12 mm
m-Xylene	1,3-dimethyl-6-crotonylbenzene	144-146/15 mm
p-Xylene	1,4-dimethylcrotonylbenzene	142-144/15 mm
	3,4,7-trimethyl-1-hydrinone	m.p. 32-33°

Reaction of Benzene with Simple Aroyl Chlorides

Optimum conditions for the reaction of aromatic hydrocarbons with aroyl chlorides are essentially the same as those used for aliphatic acid halides.

A 96-98 per cent yield of benzophenone has been obtained using the following procedure [45]:

To a mixture of 240 g of benzene, 240 g of benzoyl chloride and 400 cc of carbon bisulfide, 290 g of aluminum chloride is added. After the mixture has stood overnight, it is heated for two to three hours on a water-bath until a drop of the solution by treatment with water does not give an odor of benzoyl chloride. The whole is then treated with dilute hydrochloric acid. The carbon disulfide layer at the top is filtered, and the solvent is evaporated on the water-bath. Upon addition of alcohol to the concentrated solution, the benzophenone (m.p. 47-48°) separates out after cooling.

[39] C. Moureu, *Bull. soc. chim. (3)*, 9, 568-576 (1893); *J. Chem. Soc Abs*, 66 (I), 30 (1894).
[40] E. P. Kohler, *Am. Chem. J.*, 42, 375-401 (1909); *J. Chem. Soc. Abs.*, 96 (I), 988 (1909).
[41] G. Darzens, *Compt. rend.*, 189, 766-768 (1929); *C. A.*, 24, 542.
[42] K. v. Auwers, *Ber.*, 54, 987-1000 (1921).
[43] L. I. Smith and W. W. Prichard, *J. Am. Chem. Soc.*, 62, 770-777 (1940).
[44] K. von Auwers and E. Risse, *Ann.*, 502, 282-299 (1933); *C. A.*, 27, 1470.
[45] J. F. Norris, R. Thomas and B. M. Brown, *Ber.*, 43, 2940-2959 (1910)

Rubidge and Qua[46] reported that in the preparation of benzophenone, reducing the amount of aluminum chloride reduces the yield in almost the same proportion.

Perrier,[47] assuming the primary formation of a complex from the catalyst and acyl chlorides, recommends first the addition of aluminum chloride to benzoyl chloride and subsequent addition of benzene to this "catalyst complex."

p-Toluoyl chloride with benzene and aluminum chloride gives phenyl *p*-tolyl ketone.[48] From *p*-tolylacetyl chloride and benzene, ω-*p*-tolylacetophenone, $CH_3.C_6H_4.CH_2CO.C_6H_5$, is produced.[49] 4-Isopropylbenzoyl chloride and benzene yield 4-isopropylbenzophenone, $(CH_3)_2CH.C_6H_4.COC_6H_5$, b.p. 334-336°.[50]

By reacting α-naphthoyl chloride with benzene and aluminum chloride in carbon disulfide, α-benzoylnaphthalene is obtained.[51]

The condensation of the chloride of 1- or 2-anthraquinonecarboxylic acid with benzene was studied by Schaarschmidt,[52] who reported that the corresponding 1- and 2-benzoylanthraquinones are formed. The chloride of the 2-anthraquinonecarboxylic acid condenses readily with aromatic hydrocarbons with satisfactory results; but the isomeric chloride derived from 1-anthraquinonecarboxylic acid and, in a still more marked manner, the resulting 1-benzoylanthraquinone are very sensitive toward aluminum chloride, so that the yield is poorer.

Benzene with fluorenone-5-carboxylic acid chloride gives benzoyl-5-fluorenone, m.p. 95°.[53]

Reaction of Monohalogenated Benzene with Unsubstituted Monocarboxylic Acid Chlorides

The reaction of chlorobenzene with acetyl chloride was reported by Collet,[54] who stated that *p*-chloroacetophenone was readily prepared by mixing together acetyl chloride, chlorobenzene, and aluminum chloride. He obtained a 55 per cent yield. The ketone was also similarly prepared by Gautier,[55] who found that it melted at 20° and had a b.p. of 232°. Straus and Ackermann[56] report a yield of 80-90 per cent of the ketone based on the amount of chlorobenzene used. To an ice-cold solution of 180 g of chlorobenzene and 154 g of acetyl chloride in 400 cc of carbon disulfide, there was added during two hours 262 g of aluminum chloride. The reaction mixture was allowed to stand for two days at room temperature and then heated for three hours on a water-bath. Judefind and Reid[57] found that the best yield of *p*-chloroacetophenone was obtained

[46] C. R. Rubidge and N. C. Qua, *J. Am. Chem. Soc.*, 36, 732-7 (1914); *C. A.*, 8, 1955.
[47] G. Perrier, *Ber.*, 33, 815-6 (1900), *J. Chem. Soc. Abs.*, 78 (I), 331 (1900).
[48] E. Ador and A. A. Rilliet, *Ber.*, 12, 2298-2303 (1879).
[49] H. Strassmann, *Ber.*, 22, 1229-1231 (1889).
[50] A. W. Smith, *Ber.*, 24, 4025-4058 (1891).
[51] G. Reddelien, *Ber.*, 46, 2718-2723 (1913).
[52] A. Schaarschmidt, *Ber.*, 48, 831-839 (1915), *J. Chem. Soc. Abs.*, 108 (I), 566 (1915).
[53] R. Götz, *Monatsh.*, 23, 27-43 (1902); *J. Chem. Soc. Abs.*, 82 (I), 372 (1902).
[54] A. Collet, *Bull. soc. chim. (3)*, 21, 68-70 (1899); *J. Chem. Soc. Abs.* (I), 690 (1899).
[55] H. Gautier, *Ann. chim. phys. (6)*, 14, 373 (1888).
[56] F. Straus and A. Ackermann, *Ber.*, 42, 1813 (1909).
[57] W. L. Judefind and E. E. Reid, *J. Am. Chem. Soc.*, 42, 1044-1046 (1920).

by using one mole of chlorobenzene (112 g), a 10 per cent excess of acetyl chloride (85 g) and a 10 per cent excess of aluminum chloride (150 g) in 250 g of carbon disulfide. The chlorobenzene, aluminum chloride, and solvent were put in a flask with a reflux condenser and acetyl chloride was added in 5-g portions at intervals of about half an hour. In order to start the reaction, the flask was immersed in warm water for a short time; it was subsequently kept cold with tap water in order to avoid formation of gummy products. After completion of the reaction, the mixture was heated on a water-bath to drive off the solvent. Upon decomposition of the reaction mixture with ice, the ketone separated as a heavy oil which was dried and distilled under reduced pressure.

A good yield of *p*-chloroacetophenone has been reported by Mayer, Stark, and Schön.[58]

Collet[59] reacted propionyl chloride with chlorobenzene in the presence of aluminum chloride and obtained *p*-chloropropiophenone, m.p. 35-36°.

Schweitzer[60] reacted acetyl chloride with bromobenzene in carbon disulfide solution in the presence of aluminum chloride and obtained *p*-bromoacetophenone, m.p. 51°. Schöpff[61] repeated the preparation, and by improving the method for isolating the product, he secured a 75-80 per cent yield of the ketone. Hale and Thorp[62] performed the reaction using the Perrier[63] modification of the Friedel-Crafts reaction, *i.e.*, the formation of a catalyst complex with the acetyl chloride, and subsequent reaction of the complex with the bromobenzene. They gradually treated 50 g of the acid chloride with 76.8 g of aluminum chloride, heated the mixture on a water-bath to complete formation of the addition product, and then gradually added a solution of 90 g of bromobenzene in 150 cc of carbon disulfide. The reaction mixture was heated on the water-bath until hydrogen chloride had ceased to evolve (for about six hours). After distilling off the solvent and decomposing the catalyst complex, the ketone was steam-distilled, coming off as an oil which gradually solidified upon cooling. The yield was 70 per cent of the theoretical.

Judefind and Reid[57] prepared *p*-bromoacetophenone by adding a slight excess of acetyl chloride to a solution of bromobenzene and aluminum chloride in carbon disulfide. They reported its melting point to be 50.5°. The yield of the crude ketone obtained by them was 70-80 per cent. Propionyl chloride and bromobenzene in the presence of aluminum chloride were reacted by Collet[64] who secured *p*-bromopropiophenone, m.p. 44-45°.

Iodobenzene and acetyl chloride were reacted according to the Friedel-Crafts reaction by Schweitzer,[60] who gently warmed a solution of the reactants in carbon disulfide solution with aluminum chloride and iso-

[58] F. Mayer, Otto Stark and K. Schön, *Ber.*, 65, 1333-7 (1932).
[59] A. Collet, *Compt. rend.*, 126, 1577-1579 (1898); *J. Chem. Soc. Abs.*, 74 (1), 661 (1898).
[60] R. Schweitzer, *Ber.*, 24, 550-552 (1891); *J. Chem. Soc. Abs.*, 60 (1), 684 (1891).
[61] M. Schopff, *Ber.*, 24, 3766-3770 (1891); *J. Chem. Soc. Abs.*, 62 (1), 337 (1892).
[62] W. J. Hale and L. Thorp, *J. Am. Chem. Soc.*, 35, 267 (1913).
[63] G. Perrier, *Ber.*, 33, 815-6 (1900).
[64] A. Collet, *Compt. rend.*, 126, 1577-1579 (1898); *J. Chem. Soc. Abs.*, 74 (1), 661 (1898).

lated the *p*-iodoacetophenone (m.p. 85°) by crystallization from ether. Klages [65] obtained a 75 per cent yield of the ketone by following the procedure of Schweitzer, but he isolated his product by ether extraction and purified it by vacuum distillation. Using the Perrier modification of the Friedel-Crafts reaction and working at a temperature of 30°, Böeseken [66] obtained a 70 per cent yield. Judefind and Reid prepared *p*-iodoacetophenone by slowly adding 85 g of acetyl chloride to a mixture of 204 g of iodobenzene and 150 g of aluminum chloride, using carbon disulfide as solvent. The reaction was started by gentle warming; after it had begun, the mixture was kept cold. Upon removal of the solvent and decomposition with ice water, the product obtained by them was a dark brown mass, which, when centrifuged and crystallized from 95 per cent alcohol, gave yellow crystals of *p*-iodoacetophenone, melting at 83.5°. Schweitzer, Klages, and Böeseken had reported the melting point to be 85°.

Kimura [67] criticized the method of preparation used by Judefind and Reid, saying that it resulted in a very small yield because of the abundant formation of dark-red oil upon slow addition of the acetyl chloride to the solution of iodobenzene and aluminum chloride. The more slowly was the acetyl chloride added, the smaller the yield was found to be This, he thought, was probably caused by the splitting off of iodine as a result of secondary reactions between the excess of aluminum chloride and the iodine-containing components of the reaction mixture. By mixing the three reagents beforehand in equimolecular proportions in carbon disulfide, then cautiously heating to boiling, and continuing the boiling until the evolution of hydrogen chloride was still barely perceptible, the yield of the *p*-iodoacetophenone was increased to 80-95 per cent. The ketone was isolated by extraction with ether and crystallization from alcohol. Its m.p. was found to be 85°.

The reaction product of chlorobenzene with benzoyl chloride is *p*-chlorobenzophenone, which also may be obtained by reacting chlorobenzoyl chloride with benzene. By gradually adding aluminum chloride to a mixture of 15 g of chlorobenzene and 20 g of benzoyl chloride and then heating the mixture for an hour, Wegerhoff [68] obtained a 40 per cent theoretical yield of *p*-chlorobenzophenone, m.p. 77-78°. Montagne [69] heated for one day at 100-110° a mixture consisting of 56 g of benzoyl chloride, 55 g of aluminum chloride, and 45 g of chlorobenzene. He secured an 80-90 per cent yield of *p*-chlorobenzophenone, b.p.$_{777}$ 332 Later, Montagne and Koopal [70] reported that in the reaction a small amount of *o*-chlorobenzophenone was also formed, together with the main product of the *-p*-isomer.

An 80-90 per cent yield of *p*-chlorobenzophenone was also secured by Gomberg and Cone,[71] who heated for three hours on a water-bath a mix-

[65] A. Klages, *Ber.*, 35, 2642 (1902).
[66] J. Boeseken, *Rec. trav. chim.*, 20, 196 (1901).
[67] W. Kimura, *Ber.*, 67, 894-5 (1934); *C. A.*, 28, 3064.
[68] P. Wegerhoff, *Ann.*, 252, 6 (1889).
[69] P. J. Montagne, *Rec. trav. chim.*, 26, 263-264 (1907).
[70] P. J. Montagne and S. A. Koopal, *Rec. trav. chim.*, 29, 138,143 (1910); *J. Chem. Soc.* 98, 323 (1910).
[71] M. Gomberg and L. H. Cone, *Ber.*, 39, 3278-3279 (1906).

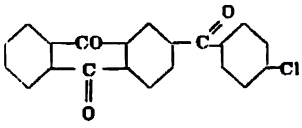
ture of 1 mole of benzoyl chloride and 2 moles of chlorobenzene with 1 mole of aluminum chloride. The temperature was then increased to 120° for two hours. When the mixture was treated with water, the crude ketone separated out. This was subsequently purified by vacuum distillation.

Cone and Long [72] reported the reaction of bromobenzene with benzoyl chloride in the presence of aluminum chloride with the production of *p*-bromobenzophenone. Using the procedure described in the preceding paragraph for their preparation of *p*-chlorobenzophenone, Gomberg and Cone likewise prepared *p*-bromobenzophenone. They found it advantageous, however, to work at temperatures lower than those used for the preparation of the chloro- compound. Here the best yields were obtained if the temperature did not exceed 80°. Montagne [73] reported that in the reaction of benzoyl chloride with bromobenzene there was formed, in addition to *p*-bromobenzophenone, a small amount of *o*-bromobenzophenone, m.p. 82.5°.

Koopal [74] heated iodobenzene with benzoyl chloride in the presence of aluminum chloride at 60° in the sunlight and secured *p*-iodobenzophenone, m.p. 102°.

o-Toluyl chloride and chlorobenzene in the presence of aluminum chloride were reacted by de Diesbach and Dobbelmann.[75] 4-Chloro-2′-methylbenzophenone (b.p. 194°/14 mm) was secured.

Schaarschmidt [76] condensed anthraquinone carboxylyl chloride with chlorobenzene in the presence of aluminum chloride to obtain 1-*p*-(chlorobenzoyl) anthraquinone,



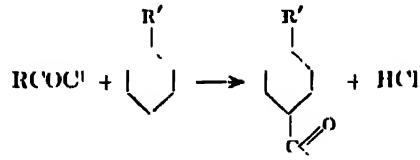
melting at 23°. A small quantity of another substance (m.p. 177°), probably its isomer, 1-*o*-(chlorobenzoyl) anthraquinone, was also obtained.

Reactions of Alkyl Benzenes with Unsubstituted Monocarboxylic Acid Chlorides

Acylation of alkyl benzenes in the presence of anhydrous aluminum chloride involves no migration of the alkyl groups present. With a few exceptions, which will be pointed out later, only mono-acylation occurs.

The acylation of mono-alkylated benzenes proceeds according to the equation:

[72] L. H. Cone and C. P. Long, *J. Am. Chem. Soc.*, **28**, 518-524 (1906).
[73] P. J. Montagne, *Rec. trav. chim.*, **27**, 336 (1908).
[74] R. A. Koopal, *Rec. trav. chim.*, **34**, 184 (1915).
[75] H. de Diesbach and P. Dobbelmann, *Helv. Chim. Acta*, **14**, 569-78 (1931).
[76] A. Schaarschmidt, *Ber.*, **48**, 831-839 (1915); *J. Chem. Soc. Abs.*, **108** (I), 566 (1915).



In acetylating toluene, xylene, and cymene Verley [77] secured an 80 per cent yield of the corresponding ketones. In order to eliminate the hydrogen chloride formed in the reaction, he carried out the condensation at 0° and in a vacuum, the acid chloride being added drop by drop to a cooled mixture of the hydrocarbon with the aluminum chloride. The use of reduced pressure in this reaction has been questioned,[78] but Verley [79] contended that, although some loss undoubtedly occurs when operating under reduced pressure with volatile compounds, like acetyl chloride, the method undoubtedly gives good yields. For example, he was able to obtain a 97 per cent yield of 2-isobutyryl-*p*-cymene by acylating *p*-cymene under reduced pressure.

It has been pointed out that in order to prevent the formation of tarry and resinous substances it is necessary to stop the reaction before its completion.[80] That conditions obviously effect yields may be appreciated by noting some of the results which have been obtained in acylating *p*-cymene. Klages and Lickroth [81] secured a 40 per cent yield of 2-acetyl-*p*-cymene. Allen,[82] recommending low temperatures and slow addition of reactants, obtained a 50-55 per cent theoretical yield. Temperatures of −5° or below were used.

The results obtained by Verley, already mentioned, show that the use of reduced pressure is significant. Both Verley and Allen employed low temperatures and added the reactants slowly. However, Verley added the acid chloride to a mixture of benzene and the catalyst, whereas Allen added the aluminum chloride to the benzene and acetyl chloride in a solvent.

That the order of addition of reactants is undoubtedly important may be emphasized by the fact that, by using Perrier's modification of the Friedel-Crafts reaction, that is, the preliminary formation of an acetyl chloride-aluminum chloride complex, a 70 per cent theoretical yield of methyl-*p*-tolyl ketone has been obtained.[83]

Addition of excess aluminum chloride after completion of the reaction has been found to increase yields. From 204 g of *n*-propylbenzene and 150 g of propionyl chloride, 196 g of *p*-propylpropiophenone has been secured.[84]

(Text cont'd. on p. 221)

[77] A. Verley, *Bull. soc. chim.*, 17 (III), 906-914 (1897); *J. Chem. Soc. Abs.*, 76 (1), 207 (1899).
[78] L. Bouveault, *Bull. soc. chim.*, 17 (III), 1020-21 (1897).
[79] A. Verley, *Bull. soc. chim.*, 19 (III), 127-140 (1898); *J. Chem. Soc. Abs.*, 76 (1), 484.
[80] A. Claus and R. Wollner, *Ber.*, 15, 1856-61 (1882); *J. Chem. Soc. Abs.*, 48, 1136 (1885).
[81] A. Klages and G. Lickroth, *Ber.*, 32, 1549-1565 (1899).
[82] C. F. H. Allen, *Organic Syntheses*, XIV, 1-3 (1934).
[83] R. Sorge, *Ber.*, 35, 1068-74 (1902).
[84] G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303-9 (1935).

Table 8. Reaction of Alkyl Benzenes with Unsubstituted Aliphatic Monocarboxylic Acid Chlorides in Presence of Anhydrous Aluminum Chloride

Hydrocarbon	Product	Reference
Toluene	4-acetyltoluene	2, 3, 16, 53
Toluene	4-propionyltoluene	26, 28
Toluene	4-butyryltoluene	28
	4-*n*-valeryltoluene	28, 30
	4-isovaleryltoluene	28
Toluene	*n*-pentadecyl *p*-tolyl ketone	27
	n-heptadecyl *p*-tolyl ketone	27, 55
Ethylbenzene	*p*-ethylpropiophenone	14
Ethylbenzene	*p*-ethylvalerophenone	30
Styrene	acylated resins	58
n-Propylbenzene	*p*-propylacetophenone	29
	p-propylpropiophenone	7
Isopropylbenzene (cumene)	*p*-isopropylacetophenone	29
tert-Butylbenzene	*p*-*tert*-butylacetophenone	31, 54
n-Octylbenzene	octylphenylmethyl ketone	36
n-Laurylbenzene	*n*-dodecylacetophenone	57
m-Xylene	2,4-dimethylacetophenone	3, 1, 5, 6
m-Xylene	diacetyl-*m*-xylene	14, 25
m-Xylene	2,4-dimethylpropiophenone	39, 56
	2,4-dimethylbutyrophenone	43
	2,4-dimethylisobutyrophenone	26, 43
	2,4-dimethylvalerophenone	30
	n-pentadecyl (2,4-dimethylphenyl) ketone	26, 27
	n-heptadecyl (2,4-dimethylphenyl) ketone	8, 50
o-Xylene	3,4-dimethylacetophenone	1, 14, 37
	3,4-dimethylisobutyrophenone	43
p-Xylene	2,5-dimethylpropiophenone	38
	2,5-dimethylbutyrophenone	43
	2,5-dimethylisobutyrophenone	43
	2,5-dimethylvalerophenone	30
	n-heptadecyl (2,5-dimethylphenyl) ketone	50, 55
m-Methylethylbenzene	2-methyl-4-ethylacetophenone	10
	2-methyl-4-ethylpropiophenone	10
	2-methyl-4-ethylisobutyrylphenone	10
	2-methyl-4-ethylbutyrylphenone	10
	2-methyl-4-ethylisovalerylphenone	10
1-Methyl-2-propylbenzene	4-methyl-3-propylacetophenone	37, 44
	4-methyl-3-propylpropiophenone	44
	4-methyl-3-propylbutyrophenone	44
1-Methyl-3-propylbenzene	4-methyl-2-propylacetophenone	43
1-Methyl-4-isopropylbenzene (*p*-cymene)	2-methyl-5-isopropylacetophenone	11, 12, 13, 14, 1, 3
	2-methyl-5-isopropylpropiophenone	48
	2-methyl-5-isopropylbutyrophenone	48
	2-methyl-5-isopropylisobutyrylphenone	16, 43
	2-methyl-5-isopropylisovalerylphenone	43

Table 8.—*Continued*

Hydrocarbon	Product	Reference
tert-Butyltoluene	2-methyl-4-*tert*-butylacetophenone	47
p-*tert*-Butyltoluene	4-*tert*-butyl-2(or 3)-acetyltoluene	34
p-Diethylbenzene	2,5-diethylacetophenone	32
1,3,5-trimethylbenzene (mesitylene)	2,4,6-trimethylacetophenone	40
	2,4,6-trimethyl-1,3-diacetylbenzene	19
	2,4,6-trimethylbutyrophenone	26
	dipropionylmesitylene	20
	2,4,6-trimethylisovalerophenone	49
	di-*n*-butyrylmesitylene	20
	di-isobutyrylmesitylene	20
	di-valerylmesitylene	20
	di-oenanthylmesitylene	20
	n-pentadecyl (2,4,6-trimethylphenyl)ketone	26, 50, 27
1,2,4-trimethylbenzene (pseudocumene)	2,4,5-trimethylacetophenone	41, 42
	2,4,5-trimethylpropiophenone	14
	2,4,5-trimethylbutyrophenone	18, 51
	2,4,5-trimethylisobutyrophenone	18, 51
	2,4,5-trimethylisovalerophenone	18, 51
1,4-dimethyl-2-ethylbenzene	1,4-dimethyl-2-ethyl-5-acetylbenzene	17
1,3-Dimethyl-4-ethylbenzene	1,3-dimethyl-4-ethyl-6-acetylbenzene	9
tert-Butyl-*m*-xylene	4-acetyl-5-*tert*-butyl-1,3-xylene	15
1,3-Dimethyl-5-*tert*-butylbenzene	2,4-dimethyl-6-*tert*-butylacetophenone	47
sym-Triethylbenzene	diacetyltriethylbenzene	14, 24
asym-Triethylbenzene	1,2,4-triethyl-5-acetylbenzene	32
1,2,4,5-Tetramethylbenzene (durene)	2,3,5,6-tetramethylacetophenone	21
	diacetyldurene	21, 22
	dipropionyldurene	21, 22
	2,3,5,6-tetramethylpropiophenone	22
1,2,3,5-Tetramethylbenzene (isodurene)	2,3,4,6-tetramethylacetophenone	22, 23
	diacetylisodurene	21, 22
1,2,3,4-Tetramethylbenzene (prehnitene)	2,3,4,5-tetramethylacetophenone	46
Ethyl mesitylene	diacetylethylmesitylene	25
Pentamethyl benzene	pentamethylacetophenone	35
1,3,5-Trimethyl-2,4-diethylbenzene	6-acetyl-1,3,5-trimethyl-2,4-diethylbenzene	23
Pentaethylbenzene	pentaethylpropiophenone	14

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Table 8.—*Concluded*

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39. A. Claus, *J. prakt. Chem. (2)*, 43, 140 (1891).
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41. A. Claus, *J. prakt. Chem. (2)*, 41, 509 (1890)
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48. A. Claus, *J. prakt. Chem. (2)*, 43, (1891), 532-536.
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The absence of extraneous solvents has been specified in a patent describing the acetylation of *tert*-butyl-*m*-xylene.[85]

As can be seen from Table 8, the orientation of the entering acyl radical is regular. Acylation of mono-alkylated benzene occurs in the *p*-position. Essner and Gossin [86] reported the ketone secured by them in reacting toluene with acetyl chloride to be *m*-tolyl methyl ketone; but it has subsequently been shown that this product was really the *p*-derivative.[87]

In the polyalkylated benzenes the entering acyl group goes into the following position in the benzene ring:

Compound	Position of Entering Acyl Group
1,2-dialkylbenzene	—4
1,3-dialkylbenzene	—4
1,4-dialkylbenzene	—6
1,3,5-trialkylbenzene	—2
1,2,4-trialkylbenzene	—5
1,2,3,4-tetralkylbenzene	—5
1,2,4,5-tetralkylbenzene	—3

[85] U. S. P. 2,047,656 (1936) to E. I. du Pont de Nemours & Co.; *C. A.*, 30, 6012.
[86] J. C. Essner and E. Gossin, *Bull. soc. chim. (2)*, 42, 95-98 (1884); *J. Chem. Soc. Abs.*, 48, 252 (1885).
[87] A. Verley, *Bull. soc. chim. (3)*, 17, 906-914 (1897); *J. Chem. Soc. Abs.*, 76 (I), 207 (1899).

In the acylation of aromatic hydrocarbons it is generally impossible to introduce two acyl groups into the aromatic nucleus by the Friedel-Crafts method. However, it has been found that diacyl derivatives of polyalkylated benzenes may be obtained according to the conditions of the reaction.[88] In spite of the fact that a ketone group inhibits further substitution, alkyl groups generally activate the remaining positions on the ring sufficiently to bring about further acylation.

The reaction time has a decided influence. When 1 g of durene was heated with 2.5 g of propionyl chloride and the required excess of catalyst for 15-20 minutes on a water-bath, dipropionyldurene was obtained. If, however, the heating was continued for one hour, the mono-acylated derivative was secured.

Benzene and ortho- or para-xylene do not under any circumstances yield diacetyl derivatives. However, meta-xylene gives approximately 2.3 per cent of the diacetyl compound, on repeating the operation several times, a large quantity of this compound can be obtained. From the experimental data, it follows that, in a compound containing an acetyl group in *ortho* position to two methyl groups, a further acetyl group can be made to enter. Since the normal acetylation product of *m*-xylene 1,3-dimethyl-4-acetylbenzene, does not contain such a grouping, the formation of the diacetyl compound in this case can be explained only by the formation of a small quantity of 1,3-dimethyl-2-acetylbenzene in the acetylation of *m*-xylene.

sym-Triethylbenzene[89] and ethylmesitylene[90] readily yield diacetyl derivatives.

Mesitylene, durene, and isodurene are instances in which an acetyl group can enter between two pairs of methyl groups; these compounds, therefore, yield 100 per cent of the diacetyl derivative on further acetylation. Since pseudocumene is acetylated only between one pair of methyl groups, it cannot be further acetylated.[90]

The acylation of alkylated benzenes has been used in the preparation of polyalkylated hydrocarbons. *n*-Alkylbenzenes are often prepared by reduction of corresponding ketones, according to Darzens.[91]

Numerous polyalkylated ketones are used in the manufacture of synthetic perfumes; for example, acetylated *tert*-butylxylene is used in the preparation of artificial musk.[92]

Alkylation and acylation have been effected in one step by treating an aromatic hydrocarbon with an acylating and alkylating agent in the presence of more than one mole of a Friedel-Crafts type condensing agent.[93] Examples are given:

[88] F. Baum and V. Meyer, *Ber.*, **28**, 3212-3215 (1895); *J. Chem. Soc. Abs.*, **70** (I), 228 (1896) V. Meyer, *Ber.*, **29**, 846 (1896).

[89] A. Klages and G. Lickroth, *Ber.*, **32**, 1549-1565 L. Gattermann, S. Fritz, and K. Beck, *Ber* **32**, 1122-1127 (1899).

[90] V. Meyer and G. Pavia, *Ber.*, **29**, 2564-69 (1896)

[91] G. Darzens, *Compt. rend.*, **139**, 868-870 (1904), *J Chem Soc. Abs*, **1905** (I), 66. *cf.* T. Y Ju, G. Shen, and C. E Wood, *J Inst. Petr*, **26**, 514-31 (1940)

[92] O. Gerhardt, *Reichstoffind.*, **5**, 67-9 (1930); *C. A.*, **24**, 4897.

[93] U. S. P. 2,004,069 (1935) to H. A Bruson and O. Stein (to Rohm and Haas)

amylphenyl methyl ketone, b. 121-3°/3 mm
mixed isomeric *sec*-amyltolyl methyl ketones, b. 140-160°/10 mm
mixed amylphenyl methyl ketones
butylacetophenone, b. 100-103°/3 mm
isopropylacetophenone, b. 83°/3 mm
tert-butylpropiophenone, b. 100°/3 mm
p-ethylacetophenone
amylpropiophenone, b. 148-52°/8 mm
amylbenzophenone, b. 153-8°/3 mm

Unsaturated Monocarboxylic Acid Chlorides and Alkylbenzenes

With unsaturated aliphatic acid chlorides the condensation may take an abnormal course. Acrylyl chloride and *p*-xylene with anhydrous aluminum chloride and carbon disulfide give *p*-xylyl vinyl ketone, $C_6H_3(CH_3)_2CO.CH{:}CH_2$. It boils at 180-240°/30 mm and usually crystallizes in the condensing tube. However, *p*-xylylethyl *p*-xylyl ketone, $C_6H_3(CH_3)_2CO.CH_2.CH_2.C_6H_3(CH_3)_2$, is formed together with the unsaturated ketone, and in larger proportion. It boils at 255-265°/30 mm and melts at 52°. The formation of the di-xylyl ketone may be due to the fact that the escaping hydrogen chloride unites with the vinyl ketone to form a compound such as $C_6H_3(CH_3)_2CO.CH_2CH_2Cl$, which acts on the excess of *p*-xylene.[94]

Alkyl Benzenes and Simple Aroyl Chlorides

Toluene and benzoyl chloride yield phenyl *p*-tolyl ketone in the presence of aluminum chloride.[95] Bourcet[96] used a large excess of toluene (1000 g of toluene, 50 g of aluminum chloride, and 100 g of benzoyl chloride). By adding the benzoyl chloride little by little to the mixture of toluene and aluminum chloride, the formation of by-products was avoided, and 92 per cent of the theoretical yield was obtained.

Since reactions of alkylated benzenes with simple aroyl chlorides proceed substantially as they do with aliphatic acid chlorides, these are merely summarized in Table 9, page 224.

Reactions of Halogenated Alkyl Benzenes or of Polyhalogenated Benzenes with Simple Acyl Chlorides

The extent of the reaction of monohalogenated toluenes with acyl chlorides in the presence of aluminum chloride depends upon the position of the halogen in the benzene ring. Reacting *o*-chloro- or *o*-bromotoluene with acetyl chloride and aluminum chloride in carbon disulfide, Claus[97] obtained *o*-chloro-*m*-acetyltoluene (b.p. 238-242°) and *o*-bromo-*m*-acetyltoluene (b.p. 262-264°). Schöpff[98] similarly reacted *o*-bromotoluene with acetyl chloride. For *o*-bromo-*m*-acetyltoluene, he reported a boiling point of 269-272°.

The condensation of *p*-chloro- and *p*-bromotoluenes with acetyl chlo-

[94] C. Mouren, *Bull. soc. chim. (3)*, **9**, 568-576; *J. Chem. Soc. Abs.*, **66** (I), 30 (1894).
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[96] P. Bourcet, *Monatshefte*, **28**, 1223 (1907).
[97] A. Claus, *J. prakt. Chem. (2)*, **43**, 353-383 (1891); *J. Chem. Soc. Abs.*, **60** (II), 911 (1891).
[98] M. Schopff, *Ber.*, **24**, 3766-3770 (1891); *J. Chem. Soc. Abs.*, **62** (I), 337 (1892).

Table 9.—Reactions of Alkylated Benzenes and Aroyl Chlorides in Presence of Anhydrous Aluminum Chloride

Alkyl Benzene	Aroyl Chloride	Product	Ref.
Toluene	*o*-toluyl chloride	2.4′-dimethylbenzophenone	1, 2
Toluene	anthraquinone-1-carboxylyl chloride	1-*p*-toluylanthraquinone	4
o-Xylene	benzoyl chloride	*asym*-benzoyl-*o*-xylene	11
p-Xylene	benzoyl chloride	*p*-xylyl phenyl ketone	10
m-Xylene	benzoyl chloride	2.4-dimethylbenzophenone	5, 6, 7
m-Xylene	*m*-toluyl chloride	*m*-tolyl 4-xylyl ketone	8
m-Xylene	*p*-toluyl chloride	2.4.4′-trimethylbenzophenone	9
p-Xylene	*o*-toluyl chloride	2.5,4′-trimethylbenzophenone	9
Mesitylene	benzoyl chloride	2,4,6-trimethylbenzophenone	12–14
Mesitylene	mesitylenic acid chloride	2.4,6,3′,5′-pentamethylbenzophenone	15
Pseudocumene	*p*-toluyl chloride	2.4,5,4′-tetramethylbenzophenone	25
Durene	benzoyl chloride	2,3,5,6-tetramethylbenzophenone also dibenzoyldurene	16
Isodurene	benzoyl chloride	benzoylisodurene	17
Ethylbenzene	benzoyl chloride	4-ethylbenzophenone	5
Ethylbenzene	toluyl chloride	2-methyl-5′-ethylbenzophenone	18
p-Diethylbenzene	benzoyl chloride	2.5-diethylbenzophenone	18
p-Diethylbenzene	*p*-toluyl chloride	4′-methyl-2.5-diethylbenzophenone	18
m-Methylethylbenzene	benzoyl chloride	2-methyl-4-ethylbenzophenone	19
p-Methylethylbenzene	*p*-toluyl chloride	2.4′-dimethyl-5-ethylbenzophenone	18
sym-Triethylbenzene	benzoyl chloride	2.4.6-triethylbenzophenone	20
Propylbenzene	benzoyl chloride	4-isopropylbenzophenone	21
Isopropylbenzene	benzoyl chloride	4-isopropylbenzophenone	23
p-Cymene	benzoyl chloride	2-methyl-5-isopropylbenzophenone	22, 24
p-Cymene	toluyl chloride	2.4′-dimethyl-5-isopropylbenzophenone	18
n-Octylbenzene	benzoyl chloride	phenyl (*n*-octylphenyl) ketone	26

1. W. Scharwin and Schorigin, *Ber.*, **36**, 2025-2027 (1903); *J. Chem Soc. Abs.*, **84** (I), 635 (1903).
2. W Mann, *Ber.*, **14**, 1645-1647 (1881); *J. Chem. Soc. Abs*, 1034 (1881)
3. H de Diesbach, *Helv. Chim. Acta*, **6**, 539-548 (1923), *J. Chem. Soc Abs*, 124 (I) 804 (1923).
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5. C Sollscher, *Ber*, **15**, 1680-1682 (1882)
6. K Elbs *J. prakt. Chem. (2)*, **35**, 469 (1887).
7. German P 267,271 (1913) to Aktien-Gesellschaft fur Anilin-Fabrikation· *C Z*. 1913, II, 2014.
8. C Seer *Monatsh.*, **32**, 163-186 (1911); *J. Chem Soc. Abs.*, **100** (I), 386 (1911).
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16. C Friedel, J. M. Crafts, and E. Ador, *Compt. rend.*, **88**, 880-884 (1879); *J Chem. Soc. Abs*, 713 (1879).
17. J C Essner and M. Gossin, *Bull soc. chim.*, **42**, 170-174; *J. Chem. Soc. Abs*, **48**, 253 (1885).
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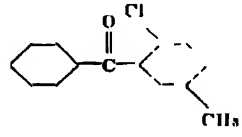
20. A Klages and G. Leckroth, *Ber.*, **32**, 1549-1565 (1899).
21. A W Smith, *Ber.*, **24**, 4023-4058 (1891).
22. A Claus *Ber*, **19**, 2879-81 (1886).
23. A Klages and P. Allendorff, *Ber*, **31**, 998-1010 (1898).
24. K Elbs, *J. prakt. Chem. (2)*, **35**, 494 (1887).
25. G T Morgan and E. A Coulson, *J Chem Soc.*, 2551-9 (1929).
26. P Lipinsky, *Ber* **31**, 938-942 (1898)

ride, according to Claus,[97] resulted in a mixture of substances. He reported, however, the formation of *o*-chloro-*m*-methylacetophenone (b.p. 239-240°) and of *o*-bromo-*m*-methylacetophenone (b.p. 257-258°). Schöpff [98] asserted, on the other hand, that no reaction occurs between para-substituted benzene halides and acyl chlorides. Thus he was able to obtain no reaction with *p*-bromotoluene. He assumed that, since the tendency of the entering acyl group is to take the position *p*- to the halogen, when the *p*-position is already occupied, no reaction occurs. For the same reason, 1-bromo-2,4-dimethylbenzene yielded no ketone upon attempted acetylation.

Heller [99] reacted *o*-chlorotoluene with benzoyl chloride. He dissolved 27 g of aluminum chloride in 32 g of *o*-chlorotoluene and, under ice-cooling, gradually added 14 g of benzoyl chloride. An 83 per cent yield of 3,4(?)-methylchlorobenzophenone (m.p. 82-83°) was obtained. With *o*-bromotoluene and benzoyl chloride, however, he was unable to obtain the corresponding ketone. The only crystalline product obtained was 3-hydroxy-4-methylbenzophenone (m.p. 173°), which was secured in 38 per cent yield. Here the chlorine atom had been replaced by a hydroxy- group. Since the condensation was effected in anhydrous media, the substitution must have occurred in the decomposition of the catalyst complex with water. Later, Heller reported that in reacting *p*-chlorotoluene with benzoyl chloride in the presence of aluminum chloride he was able to obtain from 32 g of *p*-chlorotoluene only 2.7 g of a methyl chlorobenzophenone (m.p. 35-36°). He was unable to determine the position of the substituents, but assumed for it the following structure:



It will be noticed that in the reaction of *p*-chlorotoluene with acetyl chloride, Claus [100] had also reported that the entering acyl group went *o*- to the halogen and *m*- to the methyl group.

With *p*-bromotoluene and benzoyl chloride Heller was unable to obtain any definite products, securing from 46 g of the halogenated toluene an oil which he fractionated as follows:

188-218°	7.5 g
218-260°	6 g
260-300°	4 g
15-200°/23 mm	5.5 g

Reacting *m*-bromotoluene with benzoyl chloride, he secured an oil b. 210-320°.

[98] G. Heller, *Ber.*, 46, 1497-1504 (1913); *C. A.*, 7, 2747.
[100] A. Claus, *J. prakt. Chem. (2)*, 43, 353-363 (1891); *J. Chem. Soc. Abs.*, 60 (II), 911 (1891).

A patent to Aktien-Gesellschaft für Anilin-Fabrikation [101] claims the preparation of 5-chloro-2-methylbenzophenone (b.p.$_{30}$ 210°) from *p*-chlorotoluene and benzoyl chloride by the Friedel-Crafts reaction. With 2-chlorobenzoyl chloride and *p*-chlorotoluene the preparation of 5,2′-dichloro-2-methylbenzophenone, b.$_{12}$ 225° is claimed. Here it is assumed that the acyl group enters *m*- to the halogen of the halogenated toluene. *m*-Chlorotoluene has been condensed with biphenyl-4,4′-dicarboxylyl chloride to give 4,4′-bis(*o*-methyl-*p*-chlorobenzoylbiphenyl). From 2-chloro-*p*-xylene and benzyl chloride has been obtained 2,5-dimethyl-4-chlorobenzophenone.[102]

Mayer and Fischbach[103] were able to obtain no reaction with *p*-chlorotoluene and *o*-bromomethylbenzoyl bromide. However, with *p*-bromotoluene they obtained a compound (m.p. 135°) which they considered to be either 4-bromo-1-methyl- or 1-bromo-4-methyl-anthrone. Here ring closure had been effected by displacement of both bromine atoms of the bromo-acyl bromide.

According to Böeseken,[104] dihalogenated benzene derivatives react so slowly with aluminum chloride or aluminum bromide and an acid chloride that the greater part of the acid chloride condenses with itself, so that only traces of the Friedel-Crafts condensation products are formed With acetyl chloride and *o*- and *m*-dihalogen benzenes, traces of the corresponding acetophenones were obtained, but with the *p*-dihalogen benzenes no definite product could be obtained.

The reaction involving auto-condensation of acetyl chloride has a velocity which differs widely from that of the Friedel-Crafts reaction. Böeseken [105] found that in the case of the benzene derivatives in which the substituting group increases the activity of the remaining hydrogen atoms of the benzene nucleus, the Friedel-Crafts reaction is so slow as to be practically non-existent. However, when the substituting group lessens the activity of the hydrogen atoms, the velocity of the Friedel-Crafts reaction may become equal to, or less than, that of the acetyl condensation. In the condensation of polyhalide derivatives of benzene with acetyl chloride, the velocity of the acetyl condensation is greater than that of the Friedel-Crafts reaction; therefore, only small quantities of the ketone are formed. Böeseken obtained a 2 per cent yield of dichloroacetophenone from *o*-dichlorobenzene and acetyl chloride. With *m*-dichlorobenzene only 0.4 per cent of the corresponding ketone was formed With *p*-dihalogenobenzenes no definite product could be secured. Other polyhalogenobenzenes with acetyl chloride gave no trace of ketone Schweitzer [106] reports that when *p*-diiodobenzene was treated with acetyl chloride and aluminum chloride no acetylation product could be obtained

Kunckell [107] could not effect a reaction between *p*-dichlorobenzene

[101] German P. 267,271. *J. Chem. Soc. Abs.*, 106 (I), 53 (1914); *C. Z.*, 1913, II, 2014.
[102] German P. 597,717 to I. G. Farbenindustrie.
[103] F. Mayer and W. Fischbach, *Ber.*, 58, 1251-1253 (1925); *J. Chem. Soc. Abs.*, 128 (I), 1076 (1925)
[104] J. Böeseken, *Rec. trav. chim.*, 27, 10-5 (1908); *C. A.*, 2, 1132.
[105] J. Boeseken, *Rec. trav. chim.*, 27, 10-15 (1908); *J. Chem. Soc. Abs.*, 180 (1908).
[106] R. Schweitzer, *Ber.*, 24, 550-552 (1891); *J. Chem. Soc. Abs.*, 60 (I), 584 (1891).
[107] F. Kunckell, *Ber.*, 40, 1708 (1907).

and chloroacetyl chloride with aluminum chloride and carbon disulfide, but he was easily able to introduce the chloroacetyl group into *m*-dichlorobenzene. Thus, he slowly added 20 g of aluminum chloride to a mixture consisting of 5 g of *m*-dichlorobenzene, 7 g of chloroacetyl chloride, and 50 g of carbon disulfide. There was no reaction even in sunlight; but upon being heated on a water bath the reaction began with strong evolution of hydrogen chloride. The heating was continued for one hour and the reaction mixture was then allowed to stand for three hours. He obtained 1-chloroacetyl-2,4-dichlorobenzene, $ClCH_2.CO.C_6H_3Cl_2$, m.p. 57°.

An attempt has been made to acetylate benzotrifluoride in the presence of aluminum chloride. Instead of the expected acetyl benzotrifluoride, however, there were obtained good yields of benzotrichloride and aluminum fluoride. The replacement of fluorine by aluminum chloride-chlorine without the presence of acetyl chloride yielded only a small quantity of benzotrichloride, a large amount of tar being produced.[108]

The Friedel-Crafts condensation of *o*- and *m*-dichlorobenzene with benzoyl chloride was reported by Böeseken.[109] Using aluminum chloride as catalyst and temperatures of from 110 to 140°, he secured 3,4-dichlorobenzophenone (m.p. 102°) from the *o*-halogenated compound, and 2,4-dichlorobenzophenone (m.p. 52°) from *m*-dichlorobenzophenone in 80-90 per cent yields. Similar reactions occurred with *o*- and *m*-dibromobenzene. *p*-Dichloro- or dibromobenzene was not attacked below 200°, at which temperature a black, tarry product resulted.

However, more recently, Ganzmüller [110] reported that by heating over a small flame for three days a mixture of 14.5 g of *p*-dichlorobenzene, 14.5 g of aluminum chloride and 11.5 cc of benzoyl chloride, he secured 2,5-dichlorobenzophenone. He similarly obtained 2′,2,5-trichlorobenzophenone (m.p. 145-7°) by using *o*-chlorobenzoyl chloride instead of benzoyl chloride. With 2,4-dichlorobenzoyl chloride and *p*-dichlorobenzene, he secured 2′,4′-2,5-tetrachlorobenzophenone, m.p. 176°.

The reaction of *o*-bromobenzoyl chloride and *m*-dichlorobenzene with aluminum chloride in carbon disulfide is described by Meisenheimer and co-workers,[111] who obtained a 43 per cent yield of 2-bromo-2′,4′-dichlorobenzophenone, m.p. 33-34°.

Montagne and van Charante [112] obtained 2,4-dibromobenzophenone, by the action of benzoyl chloride and aluminum chloride on *m*-dibromobenzene. Böeseken [113] likewise reacted *m*-dibromobenzene with benzoyl chloride in the presence of aluminum chloride at 170° and secured a 40 per cent yield of 2,4-dibromobenzophenone, m.p. 47°. Under the same conditions, with *o*-dibromobenzene he secured a 60 per cent yield of 3,4-dibromobenzophenone, m.p. 119°.

[108] A. L. Henne and M. S. Newman, *J. Am. Chem. Soc.*, 60, 1697-1698 (1938).
[109] J. Böeseken, *Rec. trav. chim.*, 27, 10-15 (1908); *J. Chem. Soc. Abs.*, 189 (1908).
[110] J. Ganzmüller, *J. prakt. Chem.*, 138, 311-312 (1933); *C. A.*, 28, 767.
[111] J. Meisenheimer, R. Hanseen and A. Wichterowitz, *J. prakt. Chem.*, 119, 315-367 (1928); *C. A.*, 22, 3887 (1928).
[112] P. J. Montagne and J. M. van Charante, *Rec. trav. chim.*, 31, 298-349 (1912); *J. Chem. Soc. Abs.*, 104 (I), 55 (1913).
[113] J. Böeseken, *Rec. trav. chim.*, 27, 15 (1908).

Mayer and Fischbach [114] were able to obtain no satisfactory results in an attempted reaction between *p*-dichloro- or dibromobenzene and *o*-bromomethylbenzyl bromide. Obviously, *p*-dihalogenated benzenes react much more slowly with acyl halides than the *o*- and *m*- derivatives.

The reaction of trihalogenated benzenes with benzoyl chloride and aluminum chloride has been reported by Montagne.[115] 1,3,5-Trichlorobenzene yields 2,4,6-trichlorobenzophenone, m.p. 103.5°. By heating 1,3,5-tribromobenzophenone [116] with benzoyl chloride and aluminum chloride, 2,4,6-tribromobenzophenone (m.p. 147°) was obtained.

Simple Halogenated Aliphatic Acid Chlorides and Benzene or Halogenated Benzenes

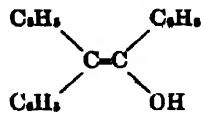
Correspondingly halogen-substituted aralkyl ketones are usually obtained by the reaction of halogen-substituted fatty acid chlorides with benzene and aluminum chloride. However, a few cases in which all the halogen has been substituted are reported. Thus, the reaction of β-chloropropionyl chloride and benzene with aluminum chloride results in the formation of either ω-phenylpropiophenone or β-chloropropionyl benzenes.[117] The same reaction has been observed between this chloride and toluene.[118]

Dichloroacetyl chloride has been reported to react in the same way. A mixture of the chloride, benzene, and aluminum chloride heated for ten hours on a water-bath yielded diphenylacetophenone, each of the chlorine atoms being substituted by a phenyl residue.[119] However, a thorough investigation of the behavior of a number of other halogenated acid chlorides when treated with benzene in the presence of aluminum chloride has shown that however the experimental conditions may be varied, only the chlorine atom attached to the carbonyl group enters into the reaction.[120] It seems that the chlorinated acid chlorides permitting polysubstitution are exceptions to the rule.

Chloroacetyl chloride and benzene heated with aluminum chloride at ordinary temperatures, or at the boiling point, give only chloroacetophenone. Even when the reaction mixture is treated with more benzene and aluminum chloride, no further addition of benzene occurs.[121]

However, the reaction of trichloroacetyl chloride with benzene in the presence of anhydrous aluminum chloride has been shown to take an unusual course. Delacre [122] reported in this way the formation of only a substance (m.p. 135° and b.p. 270-280°/40 mm), which he assumed to be diphenylacetophenone, $(C_6H_5)_2CH.CO.C_6H_5$. Later, Anschütz and Förster [123] showed that this product was in reality triphenylvinyl alcohol,

[114] F. Mayer and W. Fischbach, *Ber.*, **58**, 1251-1253 (1925); *J. Chem. Soc. Abs.*, **128** (I), 1076 (1925)
[115] P. J. Montagne, *Rec. trav. chim.*, **26**, 273-284 (1907); *J. Chem. Soc. Abs.*, 1907 (I), 855.
[116] P. J. Montagne, *Rec. trav. chim.*, **27**, 327-350 (1908); *J. Chem. Soc. Abs.*, **94** (I), 988 (1908)
[117] F. Mayer and L. van Zütphen, Dissertation, Frankfurt (1923).
[118] F. Mayer and W. Fischbach, *Ber.*, **58**, 1251-1258 (1925).
[119] A. Collet, *Bull. soc. chim.* (3), **15**, 22-23 (1896); *J. Chem. Soc. Abs.*, **72** (I), 73 (1897)
[120] A. Collet, *Bull. soc. chim.* (3), **17**, 66-80 (1897); *J. Chem. Soc. Abs.*, **74**, (I), 477 (1898).
[121] A. Collet, *Bull. soc. chim.* (3), **17**, 506-510 (1897); *J. Chem. Soc. Abs.*, **76**, 55-56 (1899).
[122] M. Delacre, *Bull. soc. chim.* (3), **13**, 357-362 (1895); *J. Chem. Soc. Abs.*, **70** (I), 455 (1896).
[123] R. Anschütz and P. Förster, *Ann.*, **362**, 89-94 (1909).



More recently, Biltz [124] reported that trichloroacetyl chloride and benzene with anhydrous aluminum chloride give triphenylvinyl alcohol, but that if moist aluminum chloride is used, the reaction product is trichloroacetophenone.

A 90 per cent theoretical yield of β-chloropropiophenone has been reported by heating under reflux a mixture of β-chloropropionyl chloride, benzene, and 1 mole of aluminum chloride.[125]

Chloroacetyl chloride and bromoacetyl chloride in the presence of aluminum chloride were reported by Collet [126] to react readily with chloro- or bromobenzene. The reactants used and products obtained were as follows:

Halogenated benzene	Acid Chloride	Product	m.p.
chlorobenzene	chloroacetyl chloride	4-chloro-ω-chloroacetophenone	101-102°
chlorobenzene	bromoacetyl chloride	4-chloro-ω-bromoacetophenone	96- 96.5°
bromobenzene	chloroacetyl chloride	4-bromo-ω-chloroacetophenone	116-117°
bromobenzene	bromoacetyl chloride	4-bromo-ω-bromoacetophenone	109-109.5°

Table 10.—Reaction of Benzene with Simple Halogenated Aliphatic Acid Halides

Acid Halides	Product	Ref.
Chloroacetyl	ω-chloroacetophenone	1, 13
Bromoacetyl	ω-bromoacetophenone	4
Dichloroacetyl	diphenylacetophenone	2
Dichloroacetyl	ω,ω-dichloroacetophenone	10
Trichloroacetyl	ω,ω,ω-trichloroacetophenone	10
Trichloroacetyl	triphenylvinyl alcohol	15, 16
β-Chloropropionyl	β-chloropropiophenone	3, 11, 12
	ω-phenylpropiophenone	11
α-Bromopropionyl	phenyl α-bromoethyl ketone	5, 7, 14
β-Iodopropionyl	β-iodopropiophenone	12
α-Bromobutyryl	α-bromobutyrophenone	6
α-Bromoisobutyryl	α-bromoisobutyrophenone	4
α-β-Dibromobutyryl	α,β-dibromobutyrophenone	9
α-Bromoisovaleryl	α-bromoisovalerophenone	8
α,α-Dibromoisovaleryl	α,α-dibromoisovalerophenone	9

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1. A. Collet, *Bull. soc. chim. (3)*, 17, 506-510 (1897); *J. Chem. Soc. Abs.*, 76, 55-56 (1899).
2. A. Collet, *Bull. soc. chim. (3)*, 15, 22-23 (1896); *J. Chem. Soc. Abs.*, 72 (I), 73 (1897).
3. J. B. Conant and W. R. Kerner, *J. Am. Chem. Soc.*, 46, 232-252 (1924); *J. Chem. Soc. Abs.*, 126 (I), 273 (1924).
4. A. Collet, *Bull. soc. chim.*, 17 (3), 66-80 (1897); *J. Chem. Soc. Abs.*, 74 (I), 477 (1898).
5. A. Collet, *Bull. soc. chim.*, 15 (3), 715-717 (1896); *J. Chem. Soc. Abs.*, 72 (I), 344 (1897).
6. A. Collet, *Bull. soc. chim.*, 15 (3), 1100-1108 (1896); *J. Chem. Soc. Abs.*, 72 (I), 823 (1897).
7. F. Kunckell, *Ber. deuts. pharm. Ges.*, 22, 180-99; *Chem. Zentr.*, 1912 (I), 1557-8.
8. F. Kunckell and K. A. Stahel, *Ber.*, 37, 1087-1090 (1904); *J. Chem. Soc. Abs.*, 86 (I), 386 (1904).
9. E. Kohler, *Am. Chem. J.*, 42, 375-401 (1909); *J. Chem. Soc. Abs.*, 96 (I), 938 (1909).
10. H. Gautier, *Ann. chem. (6)*, 14, 347-396.
11. F. Mayer and L. van Zütphen, Dissertation, Frankfurt, 1923.
12. W. J. Hale and E. C. Britton, *J. Am. Chem. Soc.*, 41, 841-7 (1919).
13. C. Friedel and J. Crafts, *Ann. chim. phys. (6)*, 1, 507.
14. F. Kunckell and Dettmar, *Ber.*, 36, 771.
15. M. Delacre, *Bull. soc. chim. (3)*, 13, 857-862 (1895).
16. R. Anschütz and P. Förster, *Ann.*, 362, 89-94 (1909).

[124] H. Biltz and co-workers, *J. prakt. Chem. (2)*, 142, 193-200 (1935).
[125] W. J. Hale and E. C. Britton, *J. Am. Chem. Soc.*, 41, 841-847 (1919).
[126] A. Collet, *Compt. rend.*, 125, 717-719 (1897); *J. Chem. Soc. Abs.*, (I), 74, 139 (1898).

Collet [127] also described the reaction of α-bromopropionyl chloride on chlorobenzene or bromobenzene in the presence of aluminum chloride. With chlorobenzene he secured *p*-chlorophenyl bromoethyl ketone (m.p. 77.5°) and with bromobenzene, *p*-bromophenyl bromoethyl ketone (m.p. 84-84.5°).

Kohler [128] reacted α,β-dibromopropionyl chloride with bromobenzene in the presence of aluminum chloride. 4-Bromophenyl α,β-dibromoethyl ketone, $CH_2Br.CHBr.CO.C_6H_4Br$ (m.p. 74°) was obtained.

Some of the halogenated aralkyl ketones prepared by reacting halogenated fatty acid chlorides with benzene and aluminum chloride are noted in Table 10, page 229.

Benzene and Halogenated Aroyl Chlorides

In the reaction of halogen-substituted aroyl chlorides with hydrocarbons, generally only the carbonyl halogen is replaced. Benzene has been reacted with the indicated halogenated aroylchloride and aluminum chloride with production of the corresponding ketone:

Table 11

Acyl Halide	Compd. Formed	m.p.	Ref
o-Bromobenzoyl chloride	*o*-bromobenzophenone	42°	1, 2, 3
p-Bromobenzoyl chloride	*p*-bromobenzophenone	82.5°	2, 4, 5
m-Bromobenzoyl chloride	*m*-bromobenzophenone	77°	3, 7
o-Chlorobenzoyl chloride	*o*-chlorobenzophenone	45.5°	9, 10
p-Chlorobenzoyl chloride	*p*-chlorobenzophenone	75–77°	14
m-Chlorobenzoyl chloride	*m*-chlorobenzophenone	82–83°	3, 8
o-Iodobenzoyl chloride	*o*-iodobenzophenone	(oxime m. at 152°)	3, 12
p-Iodobenzoyl chloride	*p*-iodobenzophenone	102°	11
p-Fluorobenzoyl chloride	*p*-fluorobenzophenone	52°	3
2,6-Dibromobenzoyl chloride	2,6-dibromobenzophenone	121.5°	13
2,4-Dibromobenzoyl chloride	2,4-dibromobenzophenone	55°	13
2,4,6-Tribromobenzoyl chloride	2,4,6-tribromobenzophenone	147°	2
4-Chloro-*o*-toluyl chloride	4-chloro-2-methylbenzophenone	41°	15

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1. W. R. Cathcart and V. Meyer, *Ber.*, 25, 1498-1500 (1892).
2. P. J. Montagne, *Rec. trav. chim.*, 27, 336-353 (1908).
3. S. A. Koopal, *Rec. trav. chim.*, 34, 115-178 (1915); *Chem. Zentr.*, 1915 (II), 332.
4. M. Schöpff, *Ber.*, 24, 3766-3770 (1891).
5. A. Schäfer, *Ann.*, 264, 152-160 (1891).
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9. P. J. Montagne and S. A. Koopal, *Rec. trav. chim.*, 29, 139 (1910).
10. B. Overton, *Ber.*, 26, 1234 (1893).
11. E. Hoffmann, *Ann.*, 264, 160-169 (1891).
12. W. Wachter, *Ber.*, 26, 1744-1748 (1893).
13. P. J. Montagne and M. van Charante, *Rec. trav. chim.*, 31, 317-337 (1912).
14. R. Demuth and M. Dittrich, *Ber.*, 23, 3609-3617 (1890).
15. H. de Diesbach and P. Dobbelmann, *Helv. Chim. Acta*, 14, 369-378 (1931).

In the preparation of monohalogenated benzophenones, it is better to react the halogenated acid chloride with benzene than the monohalogenated benzene with the acid chloride. Acid chlorides react more slowly

[127] A. Collet, 126, 1577-1579 (1898); *J. Chem. Soc. Abs.*, 74 (I), 661 (1898).
[128] E. P. Kohler, *Am. Chem. J.*, 42, 375-401 (1909); *J. Chem. Soc. Abs.*, 96 (I), 938 (1909).

with halogenated benzene than they do with halogen-free benzene.[129] However, the reaction of di- or poly-halogenated acid chlorides with benzene is so slow that better yields are obtained if di- or poly-halogenated benzene is reacted with the acid chlorides for the preparation of asymmetrically halogenated benzophenone.[130]

In the preparation of iodobenzophenone, Montagne had told Koopal [131] in a private communication that he had been able to secure the compound from *o*-iodobenzoyl chloride and benzene. Koopal was only able to secure it as the oxime, as had previously been reported by Wachter.[132]

In the reaction of halogenated aroyl chlorides with mono-halogenated benzenes, the entering acyl group generally goes *para-* to the halogen of the benzene. Thus Dittrich [130] obtained 4,4'-dichlorobenzophenone (m.p. 144-145°) from *p*-chlorobenzoyl chloride and chlorobenzene. He slowly added a mixture consisting of 40 g of the acid chloride and 32 g of chlorobenzene to 32 g of aluminum chloride in 100 g of carbon disulfide. During the addition of the reactants, and then for two days, the reaction mixture was heated on a water-bath. The yield of pure ketone was 40 g.

Montagne [133] observed that when this reaction was effected in the sunlight, 2,4'-dichlorobenzophenone (m.p. 66°) was also formed. Here the entering acyl group entered not only *para-* but also *ortho-* to the halogen. The yield of 4,4'-dichlorobenzophenone, however, had been increased to 90 per cent by working in direct sunlight.

The preparation of 2,4'-dichlorobenzophenone (m.p. 66.5-67°) from *o*-chlorobenzoyl chloride and chlorobenzene in the presence of aluminum chloride in carbon disulfide solution is described by Norris and Twieg.[134]

p-Bromobenzoyl chloride was reacted with chlorobenzene in the presence of aluminum chloride by Gomberg and Bailar,[135] who secured a 60 per cent yield of 4-chloro-4'-bromobenzophenone, m.p. 150°. They also prepared the same ketone from 4-chlorobenzoyl chloride and bromobenzene. The reaction of *p*-bromobenzoyl chloride with chlorobenzene is also described by Groves and Turner,[136] and by Bockemüller and Janssen.[137]

Chlorobenzene and ω-bromo-*o*-toluyl bromide were reacted in the presence of aluminum chloride and carbon disulfide by Mayer and Fischbach.[138] The reaction mixture was stirred for one day at room temperature. Using 20 g of the acid bromide and 8 g of chlorobenzene, there was obtained 7 g of 3-chloroanthrone, m.p. 142-144°. Here substitution of both bromo- groups occurred.

Bromobenzene and *p*-, *o*-, and *m*-bromobenzoyl chlorides have been

[129] E. Hoffmann, *Ann.*, 264, 160-169 (1891); R. Demuth and M. Dittrich, *Ber.*, 23, 3609-3617 (1890).
[130] M. Dittrich, *Ann.*, 264, 174-178 (1891).
[131] S. A. Koopal, *Rec. trav. chim.*, 34, 115-178 (1917); *C. Z.*, 1915, II, 333.
[132] W. Wachter, *Ber.*, 26, 1744-1745 (1893).
[133] P. J. Montagne, *Rec. trav. chim.*, 25, 384 (1906)
(I), 63 (1904).
[134] J. F. Norris and W. C. Twieg, *Am. Chem. Journal*, 30, 392-399 (1903). *J. Chem. Soc. Abs.*, 86
[135] M. Gomberg and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 51, 2233 (1929).
[136] L. G. Groves and E. E. Turner, *J. Chem. Soc.*, 1929, 509-511.
[137] W. Bockemüller and R. Janssen, *Ann.*, 542, 166-184 (1939).
[138] F. Mayer and W. Fischbach, *Ber.*, 58 (B), 1251-1253 (1925); *J. Chem. Soc. Abs.*, 128 (I), 1076
(1925)

reacted in the presence of aluminum chloride. Hoffmann [139] reported the formation of 4,4'-dibromobenzophenone (m.p. 172-173°) by heating gently for two days a mixture of *p*-bromobenzoyl chloride, bromobenzene, aluminum chloride and carbon disulfide. Using 12 g of the acid chloride he secured 8 g of the ketone. Montagne [140] observed that the Friedel-Crafts reaction with *p*-bromobenzoyl chloride and bromobenzene leads to the production of some 2,4'-dibromobenzophenone (m.p. 62°) in addition to the 4,4'-dibromo-compound (m.p. 175.5°) which is the chief product.

Bromobenzene was reacted with *o*-bromobenzoyl chloride by Heidenreich.[141] He diluted a mixture of the acid chloride and the bromobenzene with twice the amount of carbon disulfide, added aluminum chloride, and then gently heated the mixture on a water-bath for half an hour. He obtained a dibromobenzophenone, probably the 2,4'-dibromo-compound, and reported its melting point to be 51-52°.

Gomberg and Bailar [142] reacted *m*-bromobenzoyl chloride with bromobenzene. They heated on a steam-bath for three days a mixture consisting of 20 g of 3-bromobenzoyl chloride, 50 cc of bromobenzene, and 14 g of aluminum chloride and secured a 49 per cent yield of 3,4'-dibromobenzophenone, m.p. 132°.

The reaction of iodobenzoyl chloride with iodobenzene in carbon disulfide in the presence of aluminum chloride was found by Hoffmann [143] to give only a small yield, about 4.5 per cent, of diiodobenzophenone. Montagne [144] secured an 18 per cent yield of 4,4'-diiodobenzophenone by heating the reaction mixture at 55-60° for four days in sunlight.

Alkyl Benzenes and Halogenated Acid Chlorides

Collet [145] has reacted bromoacetyl chloride, α-bromopropionyl chloride, and α-bromobutyryl chloride with toluene and *p*-xylene in the presence of aluminum chloride. He similarly condensed chloroacetyl chloride with toluene, xylene, and mesitylene.[146] Practically all these preparations have been repeated by Kunckell,[147] who also reacted *p*-cymene, ethylbenzene, and mesitylene with some of the acid chlorides mentioned above, getting in every case (with the exception of mesitylene) monoacylation by replacement of carbonyl halogen. With mesitylene he obtained diacylation. With 1,3,5-triethylbenzene, too, diacylation was obtained if three times the theoretically necessary amount of aluminum chloride was used.[148] A number of other halogen ketones were prepared by Jacobs and

[139] E. Hoffmann, *Ann.*, 264, 163 (1891).
[140] P. J. Montagne, *Rec. trav. chim.*, 29, 156-157 (1910).
[141] A. Heidenreich, *Ber.*, 27, 1453-1456 (1894).
[142] M. Gomberg and J. C. Bailar, *J. Am. Chem. Soc.*, 51, 2232 (1929).
[143] E. Hoffmann, *Ann.*, 264, 165 (1891).
[144] P. J. Montagne, *Ber.*, 51, 1486 (1918).
[145] A. Collet, *Comptes. rend.*, 125, 805-806 (1897); *J. Chem. Soc. Abs.*, 74 (I), 478 (1898).
[146] A. Collet, *Bull. soc. chim. (3)*, 17, 506-510 (1897); *J. Chem. Soc. Abs.*, 76, 55-56 (1899).
[147] F. Kunckell, *Ber. deut. Pharm. Ges.*, 22, 180-199; *Chem. Zentr.*, 1912 (I), 1556-1558. cf. R. C. Fuson and C. H. McKeever, *J. Am. Chem. Soc.*, 62, 2062-21 (1940), for the preparation of vinyl mesityl ketone from mesitylene and β-chloropropionyl chloride.
[148] F. Kunckell, *Ber. deut. Pharm. Ges.*, 23, 188-227; *Chem. Zentr.*, 1913 (I), 1765-1770; *cf.* V. Meyer and O. Pavia, *Ber.*, 29, 2564-2569 (1896).

Heidelberger,[149] who slightly varied the methods of Kunckell and coworkers. The reaction of ethylbenzene with chloroacetyl chloride has also been described by von Auwers.[150]

Halogen-substituted aroyl chlorides react normally with alkylated benzenes and aluminum chloride. Some reactions of this type are given in Table 12.

Table 12

Alkylated benzenes	Acid Halide	Product	Ref.
Toluene	*o*-chlorobenzoyl chloride	*o*-chlorophenyl *p*-tolyl ketone	1
Toluene	*o*-bromobenzoyl chloride	*o*-bromophenyl (?)-tolyl ketone	2
Toluene	*p*-chlorobenzoyl chloride	*p*-chlorophenyl *p*-tolyl ketone	1
m-Xylene	*o*-chlorobenzoyl chloride	2,4-dimethyl-2′-chlorobenzophenone	3

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3. German P. 267,271 (1913) to Aktien-Gesellschaft für Anilin Fabrikation; *C. Z.*, 1913 (II), 2014.

Reaction of Benzene or of Benzene Homologs with Phosgene

Phosgene, $COCl_2$, is a very reactive compound and will react readily with many organic derivatives without the use of a catalyst [151]; but the addition of aluminum chloride frequently facilitates reaction. In early work on the reaction of phosgene with aromatic hydrocarbons in the presence of aluminum chloride [152] it was shown that a rapid reaction with benzene yielded benzoyl chloride and benzoic acid, but that a longer reaction time gave benzophenone:

$$C_6H_6 + COCl_2 \longrightarrow C_6H_5COCl + HCl$$

$$C_6H_5COCl \xrightarrow{H_2O} C_6H_5COOH + HCl$$

$$C_6H_6 + C_6H_5COCl \longrightarrow C_6H_5COC_6H_5 + HCl$$

Toluene reacts similarly to yield *p,p′*-ditolyl ketone.[153]

A more recent investigation of this reaction [154] has given more information on the process. It was found that the intermediate formation of a complex, $C_6H_5COCl.AlCl_3$, gave a product which could be hydrolyzed to give benzoic acid, but that this complex reacted very readily with more benzene, forming benzophenone almost entirely and without regard to operating conditions. However, if carbon disulfide was used as a solvent, a large yield of benzoic acid could be obtained because of the low solubility of the complex in carbon disulfide. The complex is thus removed from the reaction before it has time to react with more benzene to form benzophenone. The yield of benzoic acid is also increased by slowly dropping benzene into a cold mixture of carbon disulfide, phosgene, and

[149] W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, 21, 458-459 (1915); *C. A.*, 9, 2077.
[150] K. von Auwers, *Ber.*, **39**, 3757-3764 (1906); *J. Chem. Soc. Abs.*, 90 (I), 962 (1906).
[151] E. Pace, *Gazz. chim. ital.*, **59**, 576-590 (1929); *C. A.*, 24, 338.
[152] C. Friedel, J. M. Crafts, and E. Ador, *Compt. rend.*, **85**, 673-676 (1877); *Ber.*, 10, 1854-1858 (1877); *A. ch.* (6), I, 417; E. Ador and A. Rilliet, *Ber.*, 11, 399 (1878); K. Elbs, *J. prakt. Chem.* (2), **35**, 468-509 (1887); K. Elbs and G. Olberg, *Ber.*, 19, 408-410 (1886); E. Ador and J. M. Crafts, *Ber.*, 10, 2174 (1877).
[153] H. Limpricht, *Ann.*, **312**, 61-98 (1900).
[154] R. E. Wilson and E. W. Fuller, *J. Ind. Eng. Chem.*, 14, 406-409 (1922). J. F. Norris and E. W. Fuller, U. S. P. 1,543,284 (1925).

aluminum chloride, because this affords the best conditions for precipitating the $C_6H_5COCl.AlCl_3$ complex out of solution as it is formed, and before it can contact more benzene. This process gives a 90 per cent yield of pure benzoic acid.

By treating a solution of phosgene in benzene with aluminum chloride under cooling, benzophenone is obtained in 85-90 per cent yield. *m*-Xylene reacts similarly to form a di-xylyl ketone with at least two methyl groups in *ortho*- position to the carbonyl group. The addition of carbon disulfide to this reaction is not so effective in producing an acid derivative, although a small amount of a 1,3-dimethylbenzoic acid is obtained. Dipseudocumyl ketone, 2,4,5,2′,4′,5′-hexamethylbenzophenone, is also readily prepared from pseudocumene and phosgene in the presence of aluminum chloride.[155]

On the other hand, durene with phosgene and aluminum chloride at 0 to −10° gives only durene carboxylic acid; pentamethylbenzene similarly gives only the acid.[156]

Reaction of Benzene or of Benzene Homologs with Saturated Dicarboxylic Acid Chlorides

Except in the case of oxalyl chloride, reaction of saturated aliphatic dicarboxylic acid chlorides with benzene or with benzene homologs leads to production of mono- or di-ketones, depending upon the amount of hydrocarbon employed.[157]

Oxalyl Halide

Because aluminum chloride decomposes oxalyl chloride, the reaction does *not* proceed in the expected way:

$$\begin{matrix}COCl\\|\\COCl\end{matrix} + 2C_6H_6 \longrightarrow \begin{matrix}COC_6H_5\\|\\COC_6H_5\end{matrix} + 2HCl$$

or,

$$\begin{matrix}COCl\\|\\COCl\end{matrix} + C_6H_6 \longrightarrow \begin{matrix}COC_6H_5\\|\\COCl\end{matrix} + HCl$$

Instead, reaction products are similar to those obtained from phosgene or from carbon monoxide since the oxalyl chloride is decomposed into these products.

The reaction products vary with the conditions employed. Upon gradually adding 26 g of aluminum chloride to a solution of 12.7 g of oxalyl chloride in 25 cc of benzene and 50 cc of carbon disulfide there was obtained 16.2 g of benzophenone. When the reaction was conducted under strong cooling, and a carbon disulfide solution of the oxalyl chloride was slowly added to a mixture of aluminum chloride, benzene, and

[155] F. Wenzel and F. Wobisch, *Monatsh.*, 35, 987-995 (1914); *J. Chem. Soc. Abs.*, 108 (I), 561 (1915).
[156] O. Jacobsen, *Ber.*, 22, 1215-1224 (1889).
[157] A. Claus and others, *Ber.*, 20, 1874-1878 (1887); *J. Chem. Soc. Abs.*, 52, 827 (1887).

carbon disulfide, benzoyl chloride was obtained almost quantitatively, together with a small amount of benzophenone.[158]

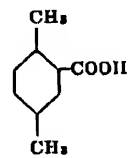
However, with oxalyl bromide, the reaction does yield some benzil, $C_6H_5CO.OCC_6H_5$, together with twice the amount of benzophenone. The formation of benzil may be explained by the fact that because oxalyl bromide is much more active than is oxalyl chloride, some of it unites with benzene before it is decomposed to carbonyl bromide and carbon monoxide.[159] The course of the reaction may, therefore, be said to be directed by the reactivity of one of the components.

The reaction of ethylbenzene with oxalyl chloride and aluminum chloride under ice-cooling with subsequent decomposition of the catalyst complex has been shown to result in the formation of *p*-ethylbenzoic acid.[160] Here the reaction conditions were substantially those used by Staudinger [161] in the preparation of benzoyl chloride from benzene and oxalyl chloride, to which reference has already been made. Production of the acid in this case was due to hydrolysis upon decomposition of the catalyst complex.

Acids were also produced adding aluminum chloride to a mixture of oxalyl chloride, carbon disulfide and toluene or one of the three xylenes under cooling, and decomposition of the catalyst complex with aqueous hydrochloric acid.[162] The following monocarboxylic acids were obtained in yields of 70-95 per cent from the indicated hydrocarbons:

Hydrocarbon	Acid
Toluene	*p*-toluic acid
o-Xylene	*o*-xylyl-4-carboxylic acid
m-Xylene	*m*-xylyl-4-carboxylic acid
p-Xylene	*p*-xylyl-2-carboxylic acid

Obviously the preferred position of the entering acid chloride residue is *para-* to a methyl substituent, unless that position is already occupied, in which case it goes *ortho-* to a methyl group. The product from *p*-xylene, obtained in almost quantitative yield, is iso-xylylic acid:



A similar reaction occurs with *p*-chlorotoluene and oxalyl chloride with aluminum chloride. Here 5-methyl-2-chlorobenzene-1-carboxylic acid (m.p. 163-166°) is obtained in 40 per cent yield. The reaction also led to the simultaneous formation of dimethyldichlorobenzophenone, due to decomposition of some of the oxalyl chloride.[163]

[158] H. Staudinger, *Ber.*, 41, 3558-3566 (1908).
[159] H. Staudinger, *Ber.*, 45, 1594-1596 (1912).
[160] A. Schonberg and O. Kraemer, *Ber.*, 55, 1174-1194 (1922).
[161] H. Staudinger, *Ber.*, 41, 3558-3566 (1908).
[162] C. Liebermann and W. Rahts, *Ber.*, 55, 1204-1205 (1922).
[163] R. Schall, K. Meyer, and A. Keller, *Ann.*, 513, 295-304 (1934); *C. A.*, 29, 1412; *cf.* Claus, *J. prakt. Chem.*, 46, 27 (1892).

Succinyl Chloride

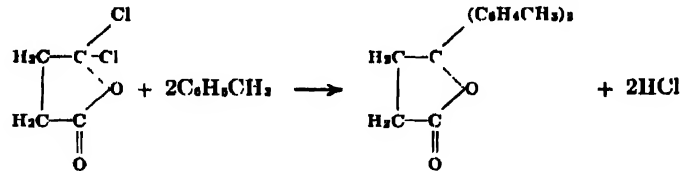
Succinyl chloride condenses with 1 mole of benzene to form β-benzoylpropionyl chloride (reaction 1) and with 2 moles of benzene to form α,β-dibenzoylethane (reaction 2).[164]

(1) $\begin{matrix}CH_2COCl\\|\\CH_2COCl\end{matrix} + C_6H_6 \longrightarrow C_6H_5COCH_2CH_2COCl + HCl$

(2) $\begin{matrix}CH_2COCl\\|\\CH_2COCl\end{matrix} + 2C_6H_6 \longrightarrow C_6H_5COCH_2CH_2COC_6H_5 + 2HCl$

Succinyl chloride may react as a lactone, in which case, γ,γ-diphenylbutyrolactone is obtained with benzene and aluminum chloride. The reaction has been studied by Auger,[165] who added aluminum chloride to a well cooled benzene solution of succinyl chloride and allowed the mixture to stand for five hours. Lutz [166] reversed the procedure. He added the acid chloride to well stirred benzene and aluminum chloride. In this way he was able to use higher temperatures and decrease the reaction time to fifteen minutes.

In reacting succinyl chloride with toluene, Limpricht [167] obtained the diketone, $C_2H_4(CO.C_6H_3CH_3)_2$ (m.p. 161°) as well as a product resulting from the reaction of the lactone form of the acid chloride and toluene, which was γ,γ-ditolylbutyrolactone,



melting at 156-157°.

Hale and Thorp [168] prepared 1,2-di-*p*-toluylethane (the diketone formed in the above reaction). A mixture of 150 g of toluene and 25 g of succinyl chloride was placed in a flask provided with a reflux condenser and gradually treated with 25 g of aluminum chloride. The mixture was warmed to 50° on a water-bath for one hour and then let stand overnight at room temperature. The contents of the flask was then treated with cold water and the excess toluene distilled off. In order to remove the lactone present the residue was warmed with a slight excess of 2 per cent sodium hydroxide. The diketone was unaffected. It may be crystallized from hot alcohol. The yield was only 2 to 3 g. owing to the fact that the greater part of the acid chloride reacts in the asymmetrical form (as the lactone).

[164] Etaix, *Ann. chim. phys. (7)*, **9**, 373 (1896).
[165] V. Auger, *Ann. chim. phys. (6)*, **22**, 310 (1891); *Bull. soc. chim. (3)*, **49**, 345 (1913).
[166] R. E. Lutz, *J. Am. Chem. Soc.*, **49**, 1106-1111 (1927).
[167] H. Limpricht, *Ann.*, **312**, 110-116 (1900).
[168] W. J. Hale and L. Thorp, *J. Am. Chem. Soc.*, **35**, 262-272 (1913).

Claus [169] prepared 1,2-di-(*m*-xyloyl)-ethane, $C_2H_4[CO.C_6H_3(CH_3)_2]_2$ (m.p. 129°) from succinyl chloride and 2 moles of *m*-xylene. Using 1 mole of the latter, β-(2,4-dimethylbenzoyl)propionic acid, $C_6H_3(CH_3)_2$-$CO.C_2H_4COOH$ (m.p. 108°) was formed. The diketone obtained from *p*-xylene melted at 123°.

Lutz [166] reacted halogenated succinyl chlorides with benzene. Here a solution of the acid chloride in benzene was added to a stirred mixture of aluminum chloride and benzene. The reactions proceeded normally:

$$\begin{matrix}CHXCOCl\\ |\\ CHXCOCl\end{matrix} + 2C_6H_6 \xrightarrow{AlCl_3} C_6H_5COCHXCHXCOC_6H_5 + 2HCl$$

Various dihalogenated *meso*- and *dl*-succinyl chlorides were reacted in this fashion. The configuration of each dihalide of dibenzoylethylene corresponds to that of the acid chloride from which it was prepared. In no case was there isolated any significant amounts of isomerized or reversed products.

Adipyl Chloride

Adipyl chloride gives with 2 moles of benzene, 1,4-dibenzoylbutane[104]:

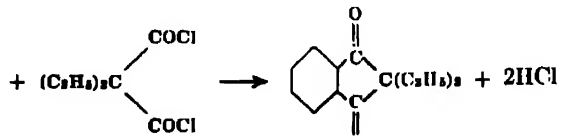
$$\begin{matrix}CH_2CH_2COCl\\ |\\ CH_2CH_2COCl\end{matrix} + 2C_6H_6 \longrightarrow \begin{matrix}CH_2CH_2COC_6H_5\\ |\\ CH_2CH_2COC_6H_5\end{matrix} + 2HCl$$

A 75-81 per cent theoretical yield of the diketone has been obtained.[169a]

Malonyl Chloride

Malonyl chloride reacts with aromatic hydrocarbons in the presence of aluminum chloride to give a diketone of the type $R.CO.CH_2COR$, a ketone of the type $R.COOH_3$, and a hydrocarbon.[169b]

The treatment of diethyl malonyl chloride with benzene [170] in the presence of aluminum chloride results in the formation of indandiones as the chief product according to the equation:

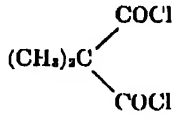


Equimolecular quantities of benzene and the chloride yield a very small amount of diethyldibenzoylmethane, $(C_6H_5CO)_2C(C_2H_5)_2$, but the

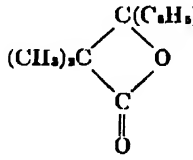
[169] A. Claus and others, *Ber.*, 20, 1374-1378 (1887); *J. Chem. Soc. Abs.*, 52, 827 (1887).
[169a] R. C. Fuson and J. T. Walker, *Organic Syntheses*, 13, 32-34 (1933); *C. A.*, 27, 3928 (1933).
[169b] A. Behal and V. Auger, *Bull. soc. chim.* (3), 9, 696-704; *J. Chem. Soc. Abs.*, 66 (I), 184 (1894).
[170] M. Freund and K. Fleischer, *Ann.*, 373, 291-336 (1910); *J. Chem. Soc. Abs.*, 98 (I), 490 (1910).

chief product is 2,2-diethylindan-1,3-dione as shown in the equation above.

The condensation of benzene with dimethylmalonyl chloride,

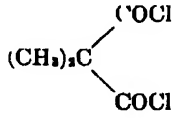


does not result in a similar formation of indandiones.[171] Instead, with equimolecular proportions of benzene and the acid chloride, there is formed chiefly isopropyl phenyl ketone, $(CH_3)_2CH.CO.C_6H_5$, besides two solid isomers, dimethyldibenzoylmethane, $(CH_3)_2C(COC_6H_5)_2$ (m.p. 125°) and the lactone of α-dimethyl-β-diphenyl-β-hydroxypropionic acid,

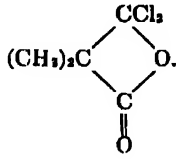


, m.p. 194°.

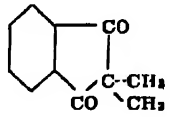
The formation of these two isomers can be explained by the fact that dimethylmalonyl chloride exists in two isomers; as an acid chloride,



or as a lactone,



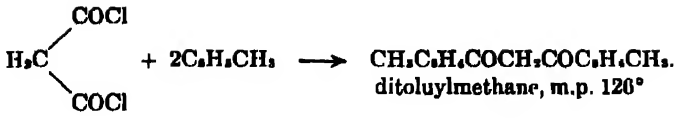
If an excess of benzene is used with the dimethylmalonyl chloride there results an oil (b.p. 230-270°) which analyzes for dimethylindandione,



and the two solid isomers noted above.

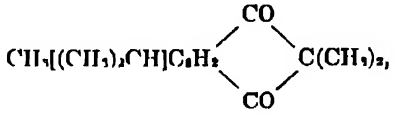
The diketone, ditoluylmethane, $CH_2(CO.C_6H_4CH_3)_2$ (m.p. 126°) is prepared from toluene and malonyl chloride:

[171] M. Freund and K. Fleischer, *Ann.*, **399**, 182-241 (1913); *C. A.*, **7**, 3737 (1913).

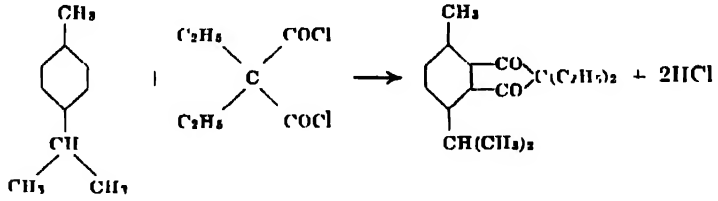


Similarly, bis-(ethylbenzoyl)methane, $CH_2(COC_6H_4.C_2H_5)_2$, was prepared from ethylbenzene. It melts at 42°. The hydrocarbon produced together with this diketone is *m*-diethylbenzene.[172] The action of 45 g of ethylmalonyl chloride on 200 g of ethylbenzene with 100 g of aluminum chloride yields the diketone $CH.C_2H_5.(CO.C_6H_4C_2H_5)_2$ (m.p. 88-89°), and *m*-diethylbenzene.[173]

The condensation of dimethylmalonyl chloride with *p*-cymene[174] in the presence of aluminum chloride gives only one product, cymenedimethylindandione,

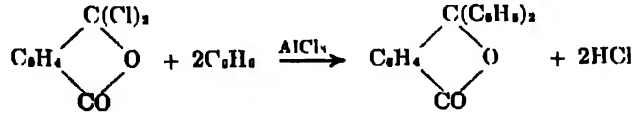


b.p. 168-169°/14 mm. Condensation of diethylmalonyl chloride with *p*-cymene[175] yielded only the corresponding ethyl derivative, cymenediethylindandione, according to the equation:



Aromatic Dicarboxylic Acid Chlorides

In reacting phthalyl chloride with benzene and aluminum chloride, Baeyer[175] reported the production of phthalophenone in yields of 80-90 per cent based on the phthalyl chloride used. Here the chloride reacts as the lactone, the reaction proceeding:



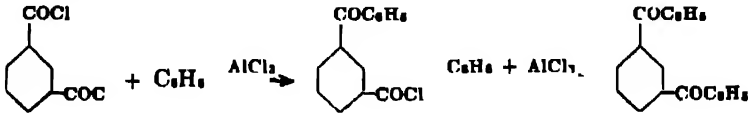
According to Haller and Guyot,[176] a small amount of 10,10-diphenylanthrone-(9) is also obtained. If an insufficient amount of aluminum

[172] A. Behal and V. Auger, *Bull. soc. chim.* (3), 9, 696-704; *J. Chem. Soc. Abs.*, 66 (I), 134 (1894).
[173] A. Behal and V. Auger, *Compt. rend.*, 110, 194-197 (1890); *J. Chem. Soc. Abs.*, 58 (I), 493 (1890).
[174] M. Freund and K. Fleischer, *Ann.*, 399, 182-241 (1913); *C. A.*, 7, 3737
[175] A. Baeyer, *Ann.*, 202, 50 (1880).
[176] A. Haller and A. Guyot, *Bull. soc. chim.* (3), 17, 873 (1897)

chloride is used, some 2-benzoylbenzoic acid is formed during the reaction.[177]

Similarly, one mole of *m*-xylene reacts with terephthalyl chloride to give 4-(2,4-dimethylbenzoyl)benzoic acid.[178]

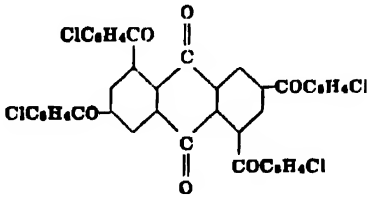
Normal condensation occurs with isophthalyl chloride and benzene, with formation of isophthalophenone.[179] The reaction takes place in two stages:



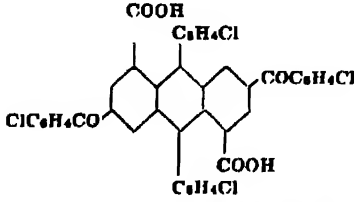
The isophthalophenone boils at 260° and melts at 99.5-100°.

When phthalic tetrachloride is dissolved in four parts of benzene and mixed with 3.5 parts of aluminum chloride, the temperature being kept at 40°, diphenylanthrone is produced. With other proportions of aluminum chloride, phenyloxanthranol and anthraquinone are formed.[180]

A tetracarboxylic acid chloride has been shown to undergo usual Friedel-Crafts condensation with chlorobenzene. Scholl, Meyer, and Keller [181] heated and slowly stirred for six hours a mixture consisting of 1.4 g of 1,3,5,7-anthraquinone carboxylyl chloride, 50 cc of chlorobenzene, and 4 g of aluminum chloride. They obtained a 28 per cent yield of 1,3,5,7-tetra-*p*-chlorobenzoylanthraquinone:



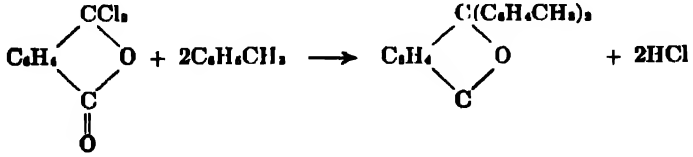
together with 1.3 per cent of 3,7-bis(*p*-chlorobenzoyl)-9,10,bis(*p*-chlorophenyl)anthracene-1,5-dicarboxylic acid:



[177] A. Haller and A. Guyot, *Compt. rend.*, 118, 140 (1894).
[178] E. Clar, F. John, and R. Avenarius, *Ber.*, 72, 2139-2147 (1939).
[179] E. Ador, *Bull. soc. chim. (2)*, 33, 56-59 (1880); *J. Chem. Soc. Abs.*, 470 (1880).
[180] A. Haller and A. Guyot, *Compt. rend.*, 121, 102-106 (1895); *J. Chem. Soc. Abs.*, 68 (I), 671 (1895).
[181] R. Scholl, K. Meyer and A. Keller, *Ann.*, 513, 205-304 (1934).

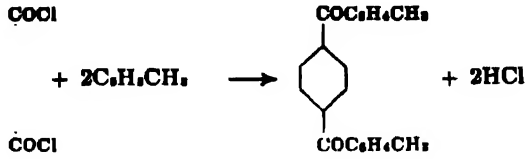
In the first case the tetracarboxylic acid chloride had reacted as an acid chloride, and in the second case as a lactone.

Toluene reacts with phthaloyl chloride to yield 3,3-di-*p*-tolyl phthalide.[182] Limpricht[183] diluted a mixture of equal parts by weight of phthalyl chloride and toluene with carbon disulfide and gradually added aluminum chloride (¾ of the weight of the phthaloyl chloride). The reaction began immediately; after all of the aluminum chloride had been added it was heated under reflux for several hours. Upon removal of the solvent, and treatment of the residue with NaOH, crystallization from alcohol gave beautiful crystals of ditolylphthalide, m.p. 116.5°. Here the phthaloyl chloride had reacted in its isomeric form:

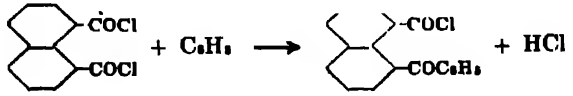


Limpricht obtained approximately a theoretical yield. Guyot[184] reported that 2-methyl-10,10-di-*p*-tolylanthrone was formed in this reaction.

Using terephthalyl chloride with toluene, Connerade[185] synthesized di-*p*-toluylbenzene (m.p. 194°) thus:



Under carefully chosen conditions, Mason[186] condensed 1,8-naphthalyl chloride with benzene to obtain a 72 per cent yield of 1-benzoyl-naphthalene-8-carboxylic acid chloride as follows:



Hydrolysis of the chloride yielded the 1-benzoylnaphthalene-8-carboxylic acid. Dicarboxylic acid chlorides of polynuclear hydrocarbons undergo similar condensation with benzene. Vollmann and co-workers[187] obtained 3,8-dibenzoylpyrene (m.p. 239°) from pyrene-3,8-dicarboxylic acid chloride and benzene, and 3,10-dibenzoylpyrene (m.p. 165°) from pyrene-3,10-dicarboxylic acid chloride and benzene. The reaction of

[182] de Berchem, *Bull. soc. chim.*, 42 (3), 168 (1884).
[183] H. Limpricht, *Ann.*, 299, 280-290 (1898).
[184] A. Guyot, *Bull. soc. chim. (3)*, 17, 968, 969 (1897).
[185] E. Connerade, *Bull. soc. chim. Belg.*, 40, 144-157 (1931); *Brit. Chem. Abs.*-A, 719 (1931).
[186] F. A. Mason, *J. Chem. Soc.*, 125, 2119-2123 (1924).
[187] H. Vollmann, H. Becker, M. Corell, H. Streeck and C. Langbein, *Ann.*, 531, 1-159 (1937); *C. A.*, 32, 145-152.

perylene dicarboxylic chlorides with benzene and toluene has been used to identify ketones prepared from perylene and benzoyl- and toluyl-chlorides.

Perylene-3,9-dicarboxylyl chloride reacts with the xylenes in the presence of aluminum chloride to give 3,9-di-xylylperylenes.[188]

The chloride of 1,1′-binaphthyl-4,4′-dicarboxylic acid condenses normally with benzene and aluminum chloride to give 4,4′-dibenzoyl-1,1′-binaphthyl, m.p. 146-147°. It is identical with the product obtained from the reaction of 1,1′-binaphthyl with benzoyl chloride and aluminum chloride.[189]

Unsaturated Dicarboxylic Acid Chlorides and Benzene or Benzene Homologs

The reaction of unsaturated dicarboxylic acid chlorides or their monoesters with aromatic compounds has received much attention, with particular reference to possible *cis-trans*- isomerization during the Friedel-Crafts reaction.

Fumaryl chloride with benzene and aluminum chloride has been reacted to give a 74 per cent yield of *trans*-dibenzoylethylene (m.p. 111°) according to the reaction:

$$ClCOCH : CHCOCl + 2C_6H_6 \xrightarrow{AlCl_3} C_6H_5COCH : CHCOC_6H_5 + 2HCl$$

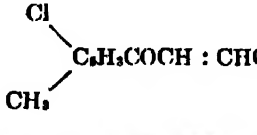
Upon replacing benzene with chlorobenzene, toluene, or mesitylene, the corresponding derivatives of dibenzoylethylene were similarly prepared. The following *trans*-diketones were thus secured[190]:

Substance	m.p.	Yield (%)
$CH_3C_6H_4COCH : CHCOC_6H_4CH_3$	148°	75
$ClC_6H_4COCH : CHCOC_6H_4Cl$	172°	51
$(CH_3)_3C_6H_2COCH : CHCOC_6H_2(CH_3)_3$	174°	75

With *m*-xylene, fumaryl chloride reacts normally in the presence of aluminum chloride to give *trans*-di-2,4-xylylethylene (m.p. 125.5-126°) in 15 per cent yield.[191]

Fumaryl chloride and *o*-chlorotoluene with aluminum chloride and carbon disulfide give a 51 per cent yield of bis(4-chloro-3-methylbenzoyl)-ethylene (m.p. 209-210°) according to the reaction:

$$ClCOCH : CHCOCl + 2ClC_6H_3CH_3 \xrightarrow{AlCl_3}$$

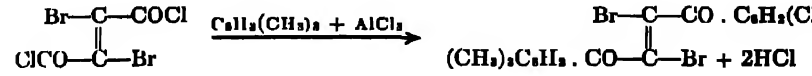


$$+ 2HCl$$

[188] A. Pongratz, *Monatsh.*, 56, 163-178 (1930); *Brit. Chem. Abstracts-A*, 1581 (1930).
[189] C. Seer and R. Scholl, *Ann.*, 398, 82-96; *C. A.*, 7, 2640 (1913).
[190] J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, 45, 1303-1307 (1923). See also R. E. Lutz *Organic Syntheses*, 20, 29-32 (1940).
[191] H. G. Oddy, *J. Am. Chem. Soc.*, 45, 2156-2160 (1923).

Bromobenzene and fumaryl chloride react in analogous manner, a 73 per cent yield of bis(4-bromobenzoyl)ethylene (m.p. 188.5°) being obtained.[192] Bromobenzene with dibromofumaryl chloride and aluminum chloride give a 60 per cent yield of *trans*-1,2-*bis*(*p*-bromobenzoyl)-1,2-dibromoethylene, m.p. 235.5°.[193]

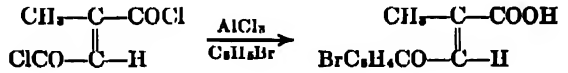
Dibromofumaryl chloride with mesitylene and aluminum chloride in carbon disulfide reacts normally, giving a 49 per cent yield of *trans*-bis-(2,4,6-trimethylbenzoyl)dibromoethylene, m.p. 198.5°:



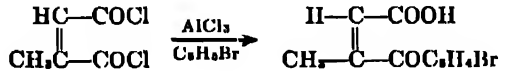
With benzene instead of carbon disulfide as solvent, the mesitylene did not react. Benzene substitution was effected, instead, and the product was *trans*-dibenzoyldibromoethylene.[194]

With bromomesitylene and fumaryl chloride in the presence of aluminum chloride and carbon disulfide, a 50 per cent yield of 1,2-bis(3-bromo-2,4,6-trimethylbenzoyl)-ethylene, $BrC_9H_{10}COCH{:}CHCOC_9H_{10}Br$ (m.p. 228-230°) has been obtained.[195]

In pursuance of this study, the Friedel-Crafts reaction with the acid chlorides of citraconic (methylmaleic acid) and mesaconic acids (methylfumaric acid) or their mono-esters has been investigated [196] in order to ascertain the influence of the methyl group on the course of the reaction. The reaction is found to proceed more readily with the *trans*-isomer than with the *cis*-compound. In the case of the acid chloride of mesaconic acid, or its mono-methyl or ethyl substituent, the reaction involves largely the carbonyl chloride which is farthest removed from the methyl, thus:



With citraconyl chloride, the carbonyl adjacent to the methyl group is largely involved, as for instance with the acid chloride of the *cis*-β-methyl acid:



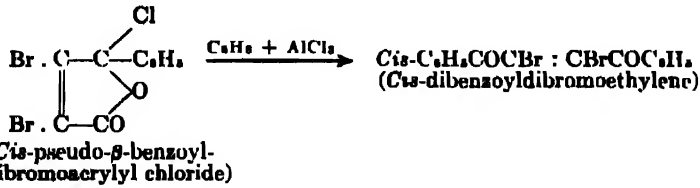
Since the yield in this case is very small, the tendency to react in the *cis*-form is not great.

The governing factor in inversion during the reaction has been shown to be the position of the methyl group.

[192] J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, 47, 881-892 (1925).
[193] R. E. Lutz and W. M. Eisner, *J. Am. Chem. Soc.*, 56, 2698-2701 (1934).
[194] R. E. Lutz, *J. Am. Chem. Soc.*, 52, 3405-3422 (1930).
[195] R. E. Lutz, E. C. Johnson and J. L. Wood, *J. Am. Chem. Soc.*, 60, 716-718 (1938); see also R. E. Lutz and C. J. Kibler, *J. Am. Chem. Soc.*, 62, 1520-1528 (1940) for reaction of dimethylfumaryl chloride with bromomesitylene.
[196] R. E. Lutz and R. J. Taylor, *J. Am. Chem. Soc.*, 55, 1168-1178 (1933). R. E. Lutz and A. W. Winne, *J. Am. Chem. Soc.*, 56, 445 (1934). R. E. Lutz, *J. Am. Chem. Soc.*, 56, 1378 (1934). R. E. Lutz, D. T. Merritt and M. Couper, *J. Org. Chem.*, 4, 95-100 (1939).

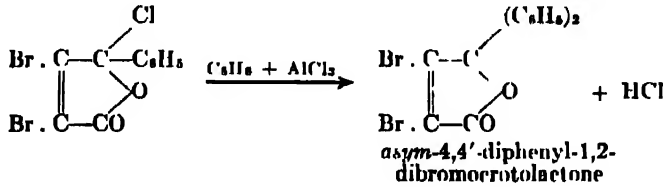
An extensive study of the Friedel-Crafts reaction with acylated acryl-yl chlorides was made by Luts.[197]

Cis-pseudo-β-benzoyldibromoacrylyl chloride was treated with aluminum chloride and benzene in a typical Friedel and Crafts reaction. It was hoped that the acid chloride would react partly to give some *cis*-dibenzoyldibromoethylene:



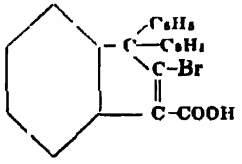
(*Cis*-pseudo-β-benzoyl-dibromoacrylyl chloride)

The reaction did not proceed in this way, however. Neither did it undergo the reaction characteristic of other lactone forms of dicarboxylic acid chlorides, which in this case should have proceeded:



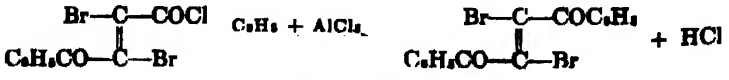
asym-4,4′-diphenyl-1,2-dibromocrotolactone

asym-4,4-Diphenyl-1,2-dibromocrotolactone may have been formed as the intermediate product, but this must have been followed by opening of the lactone ring to admit another phenyl group, and a subsequent internal condensation with loss of hydrogen bromide, for the reaction product was 1,1-diphenyl-2-bromo-3-carboxyindene,



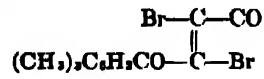
The new compound melted at 242-243° with decomposition. It was obtained in 71 per cent yield.

Treatment of *trans*-benzoyldibromoacrylyl chloride with benzene and aluminum chloride results in the formation of the expected *trans*-dibenzoyldibromoethylene in 64 per cent yield according to the reaction:



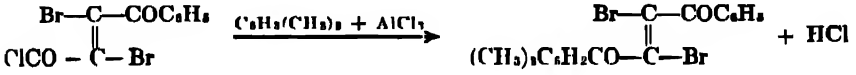
[197] R. E. Luts, *J. Am. Chem. Soc.*, 52, 3405-3422 (1930).

The reaction of *trans*-β-mesitoyldibromoacrylyl chloride with mesitylene and aluminum chloride proceeded analogously, a good yield of *trans*-dimesitoyldibromoethylene,



being obtained.

Benzoyldibromoacrylyl chloride with mesitylene and aluminum chloride in carbon disulfide gives a small yield of 1-benzoyl-2-(2,4,6-trimethylbenzoyl)-dibromoethylene (m.p. 102.5°) the reaction proceeding with normal substitution of mesitylene:



If benzene is used as the solvent, however, the benzene reacts instead of the mesitylene. In this case a good yield of *trans*-dibenzoyldibromoethylene is obtained.

Benzene and Benzene Homologs with Aralkyl Acid Chlorides

Normal substitution has been reported in the reaction of phenylacetyl chloride or its homologs with a number of alkylated benzenes in the presence of aluminum chloride, as can be seen from the following summary:

Hydrocarbon	Acid Chloride	Ketone	Ref.
Toluene	phenylacetyl chloride	*p*-tolyl benzyl ketone	1
Toluene	phenylacetyl chloride	tolyl benzyl ketone	2
Ethylbenzene	phenylacetyl chloride	benzyl (4-ethylphenyl) ketone	3
p-Xylene	phenylacetyl chloride	benzyl (2,5-dimethylphenyl) ketone	4
Mesitylene	phenylacetyl chloride	*sym*-trimethyldesoxybenzoin	5

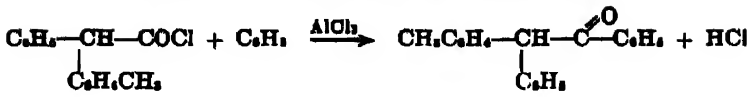
References

1. W. Mann, *Ber.*, 14, 1645-1647 (1881); *J. Chem. Soc. Abs.*, 1034 (1881).
2. J. von Braun and H. Deutsch, *Ber.*, 45, 2171-2188 (1912).
3. C. Söllscher, *Ber.*, 15, 1630-1632 (1882).
4. H. Wege, *Ber.*, 24, 3540-3543 (1891)
5. A. Klages, *Ber.*, 32, 1549-1565 (1899).

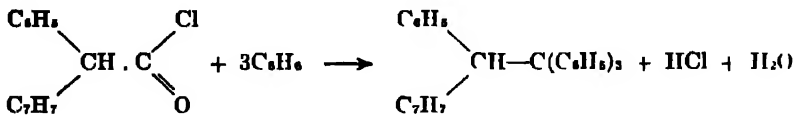
Condensation of β-phenylpropionyl chloride, $C_6H_5.CH_2CH_2COCl$, with aromatic compounds in the presence of aluminum chloride gives small yields of normal Friedel-Crafts condensation product, because of ring closure of the acid chloride.[198]

Many aralkyl acyl chlorides have been found to react with benzene and aluminum chloride in an abnormal fashion. McKenzie and Widdows [199] reported that the reaction of phenyl-*p*-tolylacetyl chloride with benzene seemed to proceed smoothly as:

[198] J. v. Braun and H. Deutsch, *Ber.*, 45, 2171-2188; *C. A.*, 6, 2027.
[199] A. McKenzie and S. T. Widdows, *J. Chem. Soc.*, 107, 702-715 (1915).

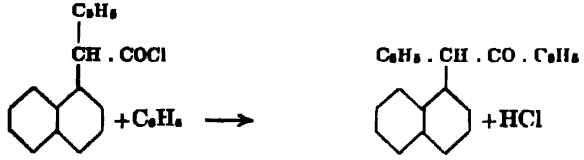


However, when Koelsch [200] tried to prepare phenyl-*p*-tolylacetophenone in this way, he was unable to do so. The only product which could be isolated was diphenylmethane. McKenzie, Roger, and McKay [201] repeated the work of McKenzie and Widdows and found that the compound thought by them to be phenyl-*p*-tolylacetyl chloride was in reality triphenyl carbinol. The reaction obviously had taken the following abnormal course:



It is possible that the tetraphenyltolylethane postulated above may have undergone scission, and that the resulting triphenylmethane was converted into its peroxide, which was subsequently hydrolyzed to triphenyl carbinol. The latter compound was obtained by these authors if the phenyl-*p*-tolylacetyl chloride used was prepared by chlorinating the corresponding acid with thionyl chloride which had been purified. If ordinary thionyl chloride was used for the chlorination, the compound obtained by the action of the acid chloride on benzene was triphenylmethane.

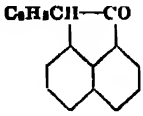
McKenzie and Tattersal [202] attempted to prepare α-naphthyldesoxybenzoin by the reaction of phenyl-α-naphthylacetyl chloride with benzene, thus:



They were unable to obtain any evidence that the action took this course. One of the products was a compound melting at 115.5-116.5°, and its analysis showed that the reaction had proceeded in an unexpected manner, since one molecular proportion of hydrogen chloride was eliminated from the acid chloride. It was thought not unlikely that an additive compound of the acetyl chloride and aluminum chloride had been formed, in which compound both the hydrogen (attached to the asymmetric carbon atom) and the chlorine of the COCl group may be more mobile than in

[200] C. F. Koelsch, *J. Am. Chem. Soc.*, 54, 2049-2052 (1932).
[201] A. McKenzie, R. Roger, and W. B. McKay, *J. Chem. Soc.*, 2597-2604 (1932).
[202] A. McKenzie and H. J. Tattersall, *J. Chem. Soc.*, 127, 2522-2530 (1925).

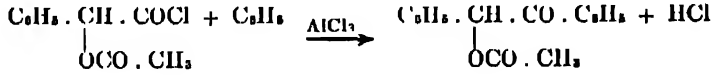
the acid chloride itself. Koelsch and Richter [203] repeated the work and showed that the compound (m.p. 115.5-116.5°) was 7-phenylacenaphthenone,



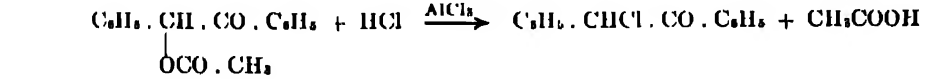
When Klingemann [204] treated diphenylacetyl chloride with benzene in the presence of aluminum chloride, he obtained a substance which he assumed was the anticipated diphenylacetophenone, but the chief product of the reaction was triphenylmethane. It was later shown [205] that the assumed diphenylacetophenone was in reality triphenylvinyl alcohol.

Triphenylvinyl alcohol has also been shown to be the product of the reaction of acetylmandelyl chloride and benzene.[206] Its formation may be explained by the following series of reactions:

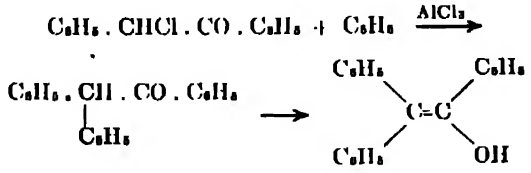
(1) The formation of acetylbenzoin:



(2) The formation of desyl chloride by the action of the evolved hydrogen chloride on acetyl benzoin:



(3) Desyl chloride, benzene, and aluminum chloride then form a ketone which immediately rearranges to triphenylvinyl alcohol:



Unsaturated Aralkyl Acid Chlorides

Unsaturated aralkyl acid chlorides have also been found to give unexpected products in reaction with benzene and aluminum chloride. Kohler and co-workers [207] obtained a hydrindone and β,β-diphenylpro-

[203] C. F. Koelsch and H. J. Richter, *J. Am. Chem. Soc.*, 59, 2165-2166 (1937); *C. A.*, 32, 532.
[204] F. Klingemann, *Ann.*, 275, 83-99 (1893).
[205] H. Biltz, *Ber.*, 32, 650-658 (1899).
[206] R. Anschütz and P. Förster, *Ann.*, 368, 90-94 (1909).
[207] E. P. Kohler, G. L. Heritage, and M. C. Burnley, *Am. Chem. J.*, 44, 60-76 (1910); *C. A.*, 4, 2637 (1910).

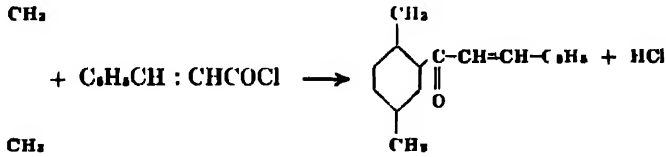
piophenone from cinnamoyl chloride and benzene; he was not able to secure styryl phenyl ketone. These results have been substantiated by von Auwers and Risse.[208]

With bromobenzene and cinnamoyl chloride, however, some normal substitution does occur. Benzal-*p*-bromoacetophenone (m.p. 100-101°), together with 6-bromo-1-phenyl-3-hydrindone, is obtained.[207] Mesitylene with cinnamoyl chloride likewise gives cinnamoylmesitylene.[209]

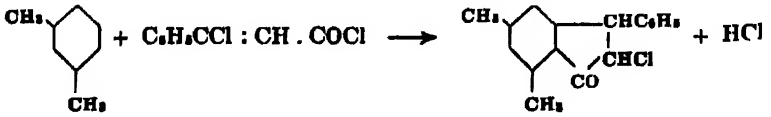
In reacting cinnamoyl chloride with benzene homologs and aluminum chloride, the following results have been obtained [208]:

Hydrocarbon	Product	m.p. (°C)
Toluene	4'-methylchalcone	76
o-Xylene	3'-4'-dimethylchalcone	72–73
m-Xylene	2',4'-dimethylchalcone	71–72
	5,7-dimethyl-3-phenyl-1-hydrindone	101
p-Xylene	4,7-dimethyl-3-phenyl-1-hydrindone	94–95

Formation of chalcone or hydrindone depends upon the presence of methyl groups on the benzene ring, so placed that they inhibit ring closure of the primarily formed chalcone. Ring closure of chalcone to hydrindone is prevented, or at least is made difficult, if there is a methyl group in the *meta*- position to the hydrogen atom in the benzene nucleus which is to be displaced upon ring closure. This is brought out in the case of *p*-xylene:

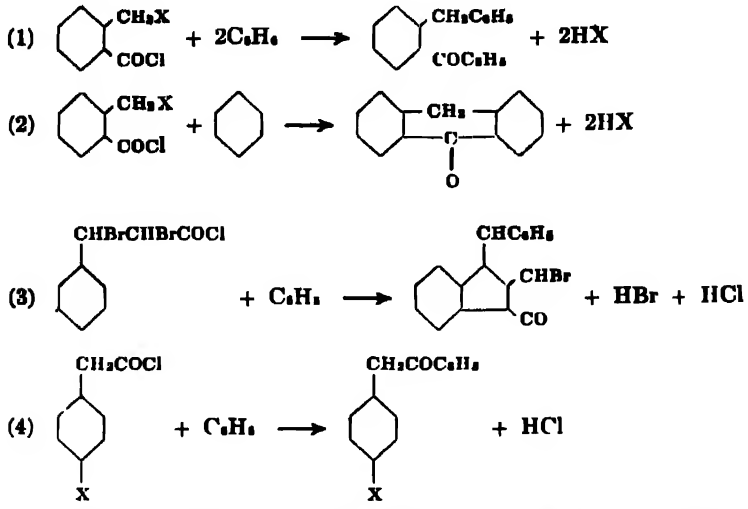


The influence of chlorine in chlorobenzal acetophenones upon ring closure has been studied. Reacting α-chloro-*trans*-cinnamoyl chloride with benzene and aluminum chloride, an 80 per cent yield of 2-chloro-3-phenyl-1-hydrindone (m.p. 94-96°) is obtained. β-Chloro-*trans*-cinnamoyl chloride similarly gives 3,3-diphenyl-1-hydrindone, the β-chlorine being replaced by phenyl during the reaction. A hydrindone was also formed from *m*-xylene and α-chloro-*trans*-cinnamoyl chloride. Here 2-chloro-3-phenyl-5,7-dimethyl-1-hydrindone was the reaction product [210]:



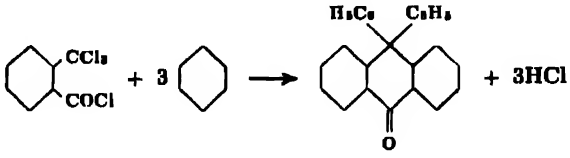
[208] K. v. Auwers and E. Risse, *Ann.*, 502, 262-299 (1933); *C. A.*, 27, 3470 (1933).
[207] E. P. Kohler, *Am. Chem. J.*, 38, 511-561 (1907); *J. Chem. Soc. Abs.*, 92, 1050 (1907).
[209] K. v. Auwers and R. Hugel, *J. prakt. Chem.*, 143, 157-178 (1935); *C. A.*, 29, 6230.

In the reaction of halogenated aralkyl acid chlorides with benzene in the presence of aluminum chloride the following types of reactions have been known to occur:



This again clearly indicates the greater activity of carbonyl halogen over the nuclear halogen.

Similar substitutions have been shown to occur in the reaction of *o*-phthalyl tetrachloride, $CCl_3.C_6H_4COCl$, in benzene solution with aluminum chloride.[211] Here diphenylanthrone (m.p. 192°) is formed:



Here 3.5 parts of aluminum chloride were used for 1 part of the tetrachloride. With other proportions of aluminum chloride, phenyloxanthrol and anthraquinone are formed.

Collet [212] reported that in the action of benzene and aluminum chloride on α-phenyl-α,β-dibromopropionyl chloride normal substitution, with formation of benzalacetophenone dibromide, occurred:

$$C_6H_5CHBrCHBrCOCl \xrightarrow{C_6H_6} C_6H_5CHBrCHBrCOC_6H_5 + HCl$$

In repeating the work, Kohler and co-workers [213] reported that the prod-

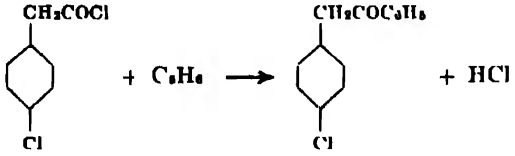
[211] A. Haller and A. Guyot, *Compt. rend.*, 121, 102-106 (1895); *J. Chem. Soc. Abs.*, 68 (I), 671 (1895).

[212] A. Collet, *Compt. rend.*, 125, 905-908 (1897); *J. Chem. Soc. Abs.*, 74 (I), 478 (1898).

[213] E. P. Kohler, G. L. Heritage, and M. C. Burnley, *Am. Chem. J.*, 44, 60-76 (1910); *C. A.*, 4, 2637 (1910).

uct was in reality 2-bromo-3-keto-1-phenyl-2,3-dihydroindene. The reaction was not one of normal acylation, but had taken place as follows:

Chlorine in the ring of aralkyl acyl chlorides is not attacked by reaction with benzene and aluminum chloride. *p*-Chlorophenylacetyl chloride gives normal substitution.[214]



Use of Miscellaneously Substituted Acyl Chlorides with Benzene and Benzene Homologs

Alkoxy-substituted Acyl Chlorides

Chlorides of alkoxy-substituted acids condense with benzene in the presence of aluminum chloride:

$$ROC_6H_4COCl + C_6H_6 \longrightarrow ROC_6H_4COC_6H_5 + HCl$$

During the reaction, the alkoxy- group may be split under the action of the aluminum chloride with formation of the corresponding hydroxyketone.

Cleavage of the methoxy- group in the reaction of the methyl ether of salicyl chloride with benzene or toluene and aluminum chloride was found to occur under ordinary conditions, *o*-hydroxybenzophenone being obtained with benzene.[215] Another substance (m.p. 127°), possibly a dihydroxybenzophenone, is formed at the same time as the monohydroxy- compound. From the acid chloride prepared from 20 g of the methyl ether of salicyclic acid and 100 cc of thiophene-free benzene with 20 g of aluminum chloride was obtained 17 g of *o*-hydroxybenzophenone. Using the chloride prepared from 8 g of the ethyl ether of salicyclic acid, only 4 g of *o*-hydroxybenzophenone was secured. Five g of salicyclic acid was formed during this reaction.[216]

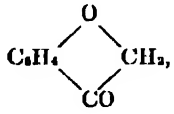
Although there is easy cleavage of the *o*-alkoxy- group, a cleavage of the alkyl groups could not be obtained by reacting *p*- or *m*-methoxybenzoyl chlorides with benzene and aluminum chloride. Here exclusively *p*- or *m*-methoxybenzophenone is formed. Thus, the chloride of anisic

[214] Petrenko-Kritschenko, *Ber.*, 25, 2239-2242 (1892)
[215] C. Graebe and F. Ullmann, *Ber.*, 29, 824-825 (1896); H. Staudinger and N. Kon, *Ann.*, 384, 90 (1911).
[216] F. Ullmann and I. Goldberg, *Ber.*, 35, 2811-2814 (1902)

acid, p-$CH_3OC_6H_4COCl$, is condensed with toluene to give a 40 per cent yield of p-tolyl p-anisyl ketone, m.p. 89°.[217]

In the reactions noted above no solvent was used. It has been reported that the use of carbon disulfide in the preparation of p-methoxybenzophenone from p-methoxybenzoyl chloride and benzene gives poor results.[218]

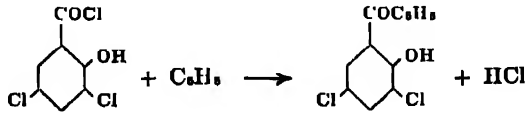
Phenoxyacetyl chloride, $C_6H_5.O.CH_2COCl$ has been reacted[219] with benzene in the presence of anhydrous aluminum chloride to give phenoxyacetophenone, $C_6H_5.O.CH_2.CO.C_6H_5$ (m.p. 72°) together with cumaranone,



resulting from ring closure of the phenoxyacetyl chloride by evolution of hydrogen chloride. Phenoxyacetyl chloride has also been condensed with toluene to give tolyl phenoxymethyl ketone, $C_6H_5.O.CH_2.CO.C_6H_4.CH_3$ (m.p. 73°), and with m-xylene to give m-xylyl phenoxymethyl ketone, m.p. 65°.

Hydroxy-substituted Acyl Chlorides

The reaction of hydroxy- acid chlorides with benzene and aluminum chloride has been studied. A 60-70 per cent yield of 3,5-dichloro-2-hydroxybenzophenone (m.p. 116°) was prepared by heating in reflux 30 g of 3,5-dichlorosalicylyl chloride, 300 g of benzene and 30 g of aluminum chloride, and subsequent treatment with dilute hydrochloric acid.



Temperatures of 30-40° were used and the reaction was completed within three or four hours.[220]

Similarly an 80 per cent yield of 3,5-dibromo-2-hydroxybenzophenone, (m.p. 129-130°) was prepared from benzene and the corresponding dibromo acid chloride.[221] The corresponding iodo- compound (m.p. 97-98°) was also prepared.[222]

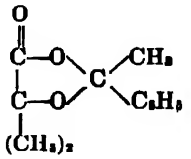
Imray[223] claims the condensation of hydroxy-aromatic acid chlorides with aromatic hydrocarbons to form hydroxydiaryl ketones. 3-Hydroxy-β-naphthoyl chloride with benzene gives phenyl 3-hydroxy-β-naphthyl

[217] A. Orekhov and J. Brouty, *Bull. soc. chim. (4)*, 47, 621-626 (1930); *Brit. Chem. Abstracts-A*, 1179 (1930).
[218] P. J. Montagne, *Rec. trav. chim.*, 40, 247-248 (1921); *C. A.*, 15, 3476.
[219] R. Stoermer and P. Atenstadt, *Ber.*, 35, 3560-3565 (1902).
[220] R. Anschütz and J. F. Shores, *Ann.*, 346, 352-356 (1906).
[221] R. Anschütz and E. Lowenberg, *Ann.*, 346, 356-359 (1906).
[222] R. Anschütz and F. Schmitz, *Ann.*, 346, 359-361 (1906).
[223] British P. 268,753 (1927) to O. Y. Imray (to I. G. Farbenindustrie); *Brit. Chem. Abstracts-B*, 276 (1928); French P. 646,402 (1928).

ketone, m.p. 161-162°. With toluene, there is similarly obtained *p*-tolyl 3-hydroxy-β-naphthyl ketone.

Ester-substituted Acyl Chlorides and Benzene or Benzene Homologs

Chlorides of acetoxy-acids have been reacted with aromatic hydrocarbons.[224] α-Acetoxyisobutyryl chloride reacts with benzene in the presence of aluminum chloride to form a mixture of phenyl α-acetoxyisopropyl ketone (m.p. 135-137°/14 mm) and the cycloacetal,



When benzene is replaced with *p*-xylene, the corresponding products, xylyl α-acetoxyisopropyl ketone (b.p. 148°/17 mm) and the expected cycloacetal were also formed. It was concluded that the chlorides of acetoxy-acids can react in two isomeric forms. One of these forms, cyclic, corresponding to the cycloacetals, isomerizes into the second, acyclic, under the influence of aluminum chloride.

The reaction of acetylglycollyl chloride with benzene in the presence of aluminum chloride results in the formation of small amounts of phenacyl alcohol and acetophenone. Here the phenyl residue combined with the cleavage product of acetylglycollyl chloride.[225]

An interesting reaction is that of benzene with ethyl chloroglyoxylate and aluminum chloride for the preparation of ethyl phenylglyoxalate, which upon hydrolysis gives phenylglyoxylic acid [226]:

$$ClOC\,.\,COOC_2H_5 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CO\,.\,COOC_2H_5 \xrightarrow{NaOH} C_6H_5CO\,.\,COOH$$

The amyl ester of benzoylformic acid has been prepared from amyl chloroglyoxylate, benzene and aluminum chloride. Toluene reacts similarly.[227]

The action of ethyl chloroglyoxylate on *p*-cymene with aluminum chloride at 10° gives cymylglyoxylic acid (b_{12} 175-180°) according to the reaction [228]:

$$\begin{matrix} COCl \\ | \\ COOC_2H_5 \end{matrix} + CH_3C_6H_4\,.\,CH(CH_3)_2 \xrightarrow{AlCl_3}$$

$$(CH_3)\,.\,CH(CH_3)_2C_6H_3CO\,.\,COOC_2H_5 \xrightarrow{NaOH}$$

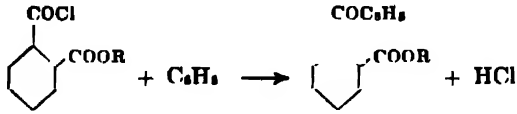
$$(CH_3)\,.\,CH(CH_3)_2\,.\,C_6H_3CO\,.\,COOH$$

[224] E. E Blaise and Herzog, *Compt rend.*, 184, 1352-1353 (1927); *Brit. Chem. Abstracts*-A, 645 (1927)
[225] R. Anschütz and P. Förster, *Ann.*, 368, 89-94 (1909); *C. A.*, 4, 155.
[226] L. Bouveault, *Bull. soc. chim. (3)*, 15, 1014-1021 (1896); *(3)*, 17, 363 (1897).
[227] L. Roser, *Ber.*, 14, 940-941 (1881).
[228] P. Chuit and J. Bolle, *Bull. soc chim. (4)*, 35, 206-205 (1924).

Ethyl adipyl chloride has been reacted [229] with benzene in the presence of aluminum chloride to give an 80 per cent theoretical yield of ethyl δ-benzoylvalerate (b.p. 164°/3 mm), according to the equation:

$$\begin{matrix} CH_2 \cdot CH_2COCl \\ | \\ CH_2 \cdot CH_2 \cdot COOC_2H_5 \end{matrix} + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CO \cdot (CH_2)_4COOC_2H_5 + HCl$$

The acid chlorides of mono-alkyl esters of aromatic dicarboxylic acids react with benzene in the presence of aluminum chloride to give ester-substituted aromatic ketones [230]:



Hydrolysis of the keto-esters gives the corresponding keto-acids.

For the above reaction, 6 g of *o*-carbomethoxybenzoyl chloride was dissolved in 80 cc of benzene, cooled to 10°, and 10 g of aluminum chloride was added gradually with shaking. After standing for one hour at room temperature, the mixture was kept at 80° for seven hours and then poured into 100 cc of 10 per cent hydrochloric acid. Upon removal of excess benzene, the ester was hydrolyzed with alcoholic potassium hydroxide. Recrystallization of the precipitate from ethyl alcohol gives 4.7 g of *o*-benzoylbenzoic acid. Equally good yields of *m*- and *p*-benzoylbenzoic acids were similarly prepared from *m*- and *p*-carbomethoxybenzoyl chlorides. The following series of reactions take place with *m*-carbomethoxybenzoyl chloride and toluene to yield *p*-toluyl-*m*-benzoic acid, m.p. 172°:

$$m\text{-}CH_3OOC \cdot C_6H_4COCl + C_6H_5CH_3 \xrightarrow{AlCl_3}$$

$$m\text{-}CH_3OOC \cdot C_6H_4COC_6H_4CH_3 \xrightarrow{KOH} m\text{-}COOH \cdot C_6H_4CO \cdot C_6H_4CH_3$$

In each case, the reaction with toluene takes place in the para-position to the methyl group. With *m*-xylene the substitution is in the *p*- position to one of the methyl groups. Here reaction with *p*- and *m*-methoxylbenzoyl chlorides gives, upon hydrolysis, 2,4-dimethylbenzoyl-*p*-benzoic and 2,4-dimethylbenzoyl-*m*-benzoic acids, respectively.

m-Carboethoxybenzoyl chloride has been found to react similarly with benzene.[231]

In order to prepare a diketone of hydroquinone, Pummerer and Buchta [232] esterify hydroquinone dicarboxylic acid, $C_6H_2(OH)_2(CO_2H)_2$, into the diacetate, $C_6H_2(OOCCH_3)_2(CO_2H)_2$, convert this into the corresponding dicarboxylyl chloride, and react it with benzene.

[229] S. Grateau, *Compt. rend.*, **191**, 947-949 (1930).
[230] M. E. Smith, *J. Am. Chem. Soc.*, **43**, 1920-1934 (1921); *C. A.*, **16**, 88.
[231] B. Samdahl and T. Christiansen, *Bull. soc. chim.* (5), **5**, 1573-1580 (1938).
[232] R. Pummerer and E. Buchta, *Ber.*, **69**, 1013-1021 (1936); *C. A.*, **30**, 4854.

Hydroxybenzophenones have often been prepared by hydrolyzing the product formed from the interaction of benzene and carbomethoxyoxybenzoic acids. Treatment in the cold of phenol acids with an alkaline solution of methyl chloroformate, $ClCOOCH_3$, results in the formation of carbomethoxyoxybenzoic acids. Thus *p*-hydroxybenzoic acid and methyl chloroformate react as follows:

$$OH.C_6H_4COOH + ClCOOCH_3 \longrightarrow CH_3OOC.O.C_6H_4COOH + HCl$$

The reaction takes place rapidly with *p*-hydroxybenzoic acid, 1,3,4-trihydroxybenzoic acid, and 3,4,5-trihydroxybenzoic acid. It proceeds difficultly, however, with *o*-hydroxybenzoic acid. With 2,5-dihydroxybenzoic and *β*-resorcylic acids, both of which have a hydroxyl group adjacent to the carboxyl radical, only one addition occurs. This is often apparent with hydroxy-acids in which a hydroxy- group is *ortho-* to the carboxyl. The derivatives are of importance because they may be easily transformed, *e.g.*, with phosphorus pentachloride, into carbomethoxyoxybenzoyl chlorides which are as active in ketone synthesis as benzoyl chloride. With benzene and aluminum chloride, carbomethoxyoxybenzophenones are formed, which may be easily saponified with cold alkalies to regenerate the original phenol groups.[233] The synthesis has been applied by Fischer [234] to the preparation of several hydroxy-ketones. *p*-Hydroxybenzophenone has been synthesized in 82 per cent yield by the following series of reactions:

$$4\text{-}OHC_6H_4COOH + ClCOOCH_3 \longrightarrow 4\text{-}CH_3OOC.O.C_6H_4COOH \xrightarrow{PCl_5}$$

$$4\text{-}CH_3OOCO.C_6H_4COCl \xrightarrow[AlCl_3]{C_6H_6}$$

$$4\text{-}CH_3OOC.O.C_6H_4COC_6H_5 \xrightarrow{NaOH} 4\text{-}OHC_6H_4COC_6H_5$$

It was hoped that the synthesis could be used in the acylation of aralkylhydroxy-acids.[235] Carbomethoxyoxymandelic acid chloride was prepared, but in the Friedel-Crafts reaction with benzene and aluminum chloride the expected benzoin was not obtained. The reaction should have proceded:

$$C_6H_5.CH(OH).COOH \xrightarrow{ClCOOCH_3} C_6H_5.CH(O.COOCH_3).COOH \xrightarrow{SOCl_2}$$

$$C_6H_5.CH(O.COOCH_3)COCl \xrightarrow{C_6H_6} C_6H_5.CH(O.COOCH_3)CO.C_6H_5 \xrightarrow{NaOH}$$
$$C_6H_5.CH(OH).CO.C_6H_5$$

Instead, a cleavage of the carbomethoxyoxy- group occurred during the reaction with benzene and aluminum chloride:

$$C_6H_5.CH(O.COOCH_3)COCl \xrightarrow{2C_6H_6} C_6H_5.CHC_6H_5.COC_6H_5 + HCl + CH_3COOH$$

[233] E. Fischer, *Ber.*, 41, 2875-2891 (1908).
[234] E. Fischer, *Ber.*, 42, 1015-1022 (1909); *Ann.*, 371, 303-319 (1910); *J. Chem. Soc. Abs.*, 98 (I), 248 (1910).
[235] A. McKenzie and M. S. Leslie, *Ber.*, 61, 153-163 (1928); *C. A.*, 22, 1334 (1928).

The corresponding ethoxyoxy- derivative behaved in the same way. The chloride of carbomethoxyoxyatrolactinic acid, $C_6H_5(CH_3)C(O.COOCH_3)$-$COCl$, gave in the Friedel-Crafts reaction, $(C_6H_5)_2C(CH_3)COOH$, an utterly unexpected product. Here the carbomethoxyoxy- group was split off as carbon dioxide; and as methyl chloride was formed by the action of hydrogen chloride, the reaction resulted in the formation of atrolactinic acid chloride, $C_6H_5(CH_3)C(OH)COCl$. Then the hydroxy- group was replaced by chlorine, also by the action of hydrogen chloride. Finally, the chlorine of the asymmetric carbon atom seemed not to be bound as fast as the chlorine of the carboxyl group, for the following occurred:

$$C_6H_5(CH_3)C(Cl).CO.Cl \xrightarrow{C_6H_6} C_6H_5(CH_3)C(C_6H_5).CO.Cl + HCl$$

In water, however, the acid chloride was changed to the acid, $CH_3.C(C_6H_5)_2.COOH$.

It will be noted that in mandelic and in atrolactinic acids the hydroxy-group is not attached directly to the benzene ring as it is in the phenol acids. This may explain the abnormal course of the reaction.

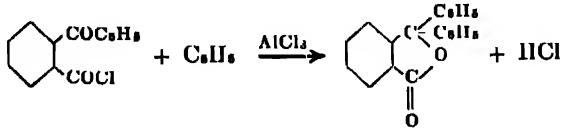
Ketonic Acid Chlorides

A few instances have been cited of the use of ketonic acid chlorides in the Friedel-Crafts condensation. Thus Limpricht[236] obtained *p*-toluyl-*p*-toluphenone, $CH_3.C_6H_4.CO.C_6H_4.CO.C_6H_4CH_3$ (m.p. 188°) by heating the chloride of *p*-toluyl-*p*-benzoic acid with aluminum chloride in toluene.

By the action of fluorenone-4-carboxylyl chloride on toluene in the presence of aluminum chloride, there is formed 4-*p*-toluylfluorenone, m.p. 128°.[237]

Acetoacetyl chloride has been shown to react with benzene and aluminum chloride to give a 27 per cent yield of the normal Friedel-Crafts reaction product, benzoylacetone.[238]

If the ketonic group is *ortho*- to the COCl group, however, ring closure may occur. Thus Meyer[239] reports that *o*-benzoylbenzoyl chloride reacts with benzene to form phthalophenone:

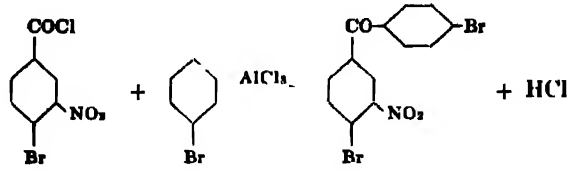


Nitro-substituted Aroyl Chlorides and Benzene or Benzene Homologs

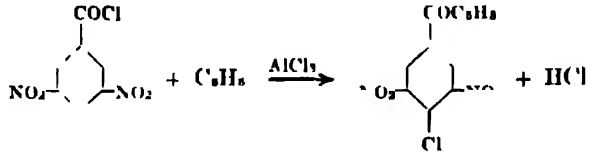
The nitro- group in the *meta*- or *para*- position of the halogenated component does not exert the inhibiting action which is displayed when it

[236] H. Limpricht, *Ann.*, 312, 91-98 (1900); *J. Chem. Soc. Abs.*, 1900 (I), 598.
[237] H. Pink, *Monatsh.*, 25, 979-986 (1904); *J. Chem. Soc. Abs.*, 88 (I), 68 (1905).
[238] C. D. Hurd and C. D. Kelso, *J. Am. Chem. Soc.*, 62, 1548-1549 (1940).
[239] H. Meyer, *Monatsh.*, 25, 1177-1195 (1904); *J. Chem. Soc. Abs.*, 88 (I), 133 (1905).

is present in the aromatic hydrocarbon which is to be substituted; *meta*- and *para*- nitroaroyl chlorides have been generally used to prepare the correspondingly substituted diaroyl ketones. The reactions occur smoothly, giving in each case the normal substitution product. For example, the product of the reaction of 4-bromo-3-nitrobenzoyl chloride with bromobenzene is the expected 4,4'-dibromo-3-nitrobenzophenone [240]:

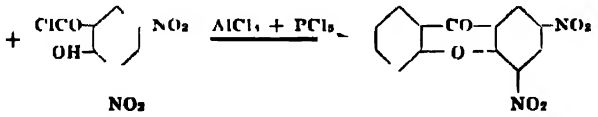


Dinitro- substitution does not affect the course of the reaction, 4-chloro-3,5-dinitrobenzoyl chloride yielding 4-chloro-3,5-dinitrobenzophenone with benzene and aluminum chloride [241]:

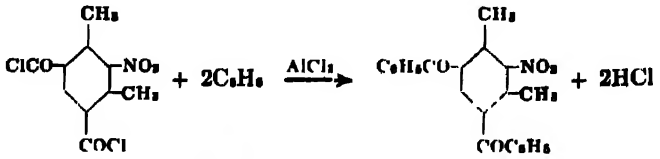


Reactions of *m*- or *p*-substituted acid chlorides with benzene or benzene homologs in which normal condensation products have been obtained are tabulated in Table 13, page 257.

An interesting reaction is that of dinitrosalicylyl chloride with benzene, phosphorus pentachloride and aluminum chloride to give 2,4-dinitroxanthone [242]:



Condensation of a nitro-substituted dicarboxylic acid with benzene may also be effected. Thus from 1,3-dimethyl-2-nitrobenzene-4,6-dicarboxylic acid chloride is obtained 2-nitro-4,6-dibenzoyl-*m*-xylene [243]:



[240] M. Schöpff, *Ber.*, 24, 3771-3784 (1891).
[241] F. Ullmann, *Ann.*, 366, 79-118 (1909).
[242] F. Ullmann, *Ann.*, 366, 87 (1909).
[243] H. de Diesbach and L. Chardonnes, *Helv. Chim. Acta*, 7, 814-818 (1924); J. *Chem. Soc.* 126 (I), 1082 (1924).

Table 13

Hydrocarbon	Acid Chloride	Ref.
Benzene	*m*-nitrobenzoyl	1, 2, 3
Benzene	6-chloro-3-nitrobenzoyl	4
Benzene	4-chloro-3-nitrobenzoyl	5
Chlorobenzene	*m*-nitrobenzoyl	6
Chlorobenzene	4-chloro-3-nitrobenzoyl	7
Benzene	4-bromo-3-nitrobenzoyl	8
Bromobenzene	3-nitrobenzoyl	6
Bromobenzene	4-bromo-3-nitrobenzoyl	10, 8
Benzene	2-chloro-3,5-dinitrobenzoyl	11
Benzene	4-chloro-3,5-dinitrobenzoyl	12
Benzene	4-methyl-3-nitrobenzoyl	13
Benzene	*p*-nitrobenzoyl	14, 15
Bromobenzene	*p*-nitrobenzoyl	16, 6
Chlorobenzene	*p*-nitrobenzoyl	16, 6
Benzene	2-iodo-4-nitrobenzoyl	17
Toluene	*m*-nitrobenzoyl	18
Toluene	*p*-nitrobenzoyl	19
m-Xylene	*m*-nitrobenzoyl	20
o-Xylene	*m*-nitrobenzoyl	20
Benzene	β-(4-nitrophenyl)-β-(9-anthron-10-yl)propionyl	21

References

1. R. Geigy and W. Koenigs, *Ber.*, **18**, 2401-2407 (1885).
2. P. J. Montagne, *Rec. trav. chim.*, **36**, 260 (1917).
3. G. J. Esselen and L. Clarke, *J. Am. Chem. Soc.*, **36**, 308-324 (1914).
4. F. Ullmann and E. Mallett, *Ber.*, **31**, 1694-1696 (1898).
5. D. Muron and C. Fox, *Ber.*, **47**, 2774-2783 (1914).
6. P. J. Montagne, *Ber.*, **49**, 2262-2276 (1916).
7. P. J. Montagne, *Rec. trav. chim.*, **21**, 25 (1902).
8. M. Schopff, *Ber.*, **24**, 3771-3784 (1891).
9. J. Boeseken, *Rec. trav. chim.*, **23**, 108 (1904).
10. P. J. Montagne, *Ber.*, **48**, 1031 (1915).
11. F. Ullmann and J. Broulo, *Ber.*, **39**, 356-369 (1906).
12. F. Ullmann, *Ann.*, **366**, 70-116 (1909).
13. R. Weiss and J. L. Katz, *Monatsh.*, **50**, 109-114 (1928); *C. A.*, **23**, 839.
14. P. Carré, *Compt. rend.*, **144**, 34 (1907); *Bull. soc. chim. (4)*, **5**, 281 (1909); *Ann. chim. phys. (8)*, **19**, 228 (1910).
15. G. Schroeter, *Ber.*, **42**, 3356-3362 (1909).
16. J. Boeseken, *Rec. trav. chim.*, **23**, 107 (1904).
17. C. Willgerodt and R. Gartner, *Ber.*, **41**, 2813-2826 (1908).
18. H. Limpricht and M. Lenz, *Ann.*, **286**, 307-320 (1895).
19. H. Limpricht and F. Samiets, *Ann.*, **286**, 321-332 (1895).
20. H. Limpricht and H. Falkenberg, *Ann.*, **286**, 333-342 (1895).
21. P. Gagnon and R. Hudon, *Trans. Roy. Soc. Canada III*, **33**, 37-46 (1939); *C. A.*, **34**, 2837.

Recently, it has been reported[244] that in spite of the inability of earlier workers[245] to obtain *o*-nitrophenyl aryl ketones from *o*-nitrobenzoyl chloride by the Friedel-Crafts reaction, they can be prepared by this method if the aluminum chloride is replaced by ferric chloride, and the condensation is effected in a suitable diluent.

Reaction with Miscellaneous N-substituted Acid Chlorides

Aroylamino-acid chlorides have been shown to undergo normal Friedel-Crafts condensation with benzene or with benzene homologs. Thus the chloride of benzoyl-ε-leucine reacts with toluene:

$$C_6H_5CO \cdot NH \cdot (CH_2)_5COCl + C_6H_5CH_3 \xrightarrow{AlCl_3}$$

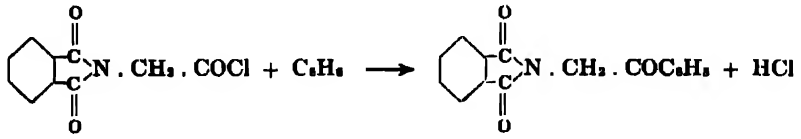
$$C_6H_5CO \cdot NH \cdot (CH_2)_5COC_6H_4 \cdot CH_3 + HCl$$

[244] M. Boëtius and H. Römisch, *Ber.*, **68**, 1934-1932 (1935).
[245] R. Geigy and W. Koenigs, *Ber.*, **18**, 2400-2407 (1885). A. Schaarschmidt and J. Hersenberg, *Ber.*, **53**, 1288-1298 (1930).

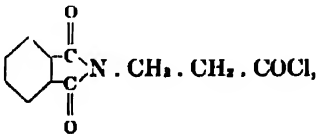
The new toluyl derivative could not be purified, but was hydrolyzed by means of fuming hydrochloric acid and converted into tolyl ε-amino-amyl ketone hydrochloride.[246]

Benzene and the chloride of benzoyl-ε-leucine gives the expected ε-benzamidocaprophenone (m.p. 95°) by like procedure.[247]

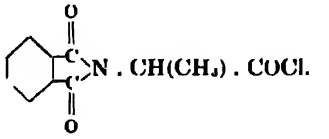
Phthalylglycyl chloride and its homologs have been shown to react with benzene and anhydrous aluminum chloride, the acid chlorine being replaced by a phenyl group with formation of ketones [248]:



Hydrolysis yields aminoalkyl aryl ketones. Similarly, β-phthalylalanyl chloride,

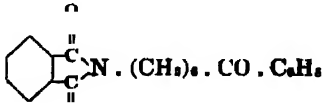


gives β-phthalimidopropiophenone,[249] and α-phthalimidopropiophenone is obtained by using the isomeric phthalylalanyl chloride,



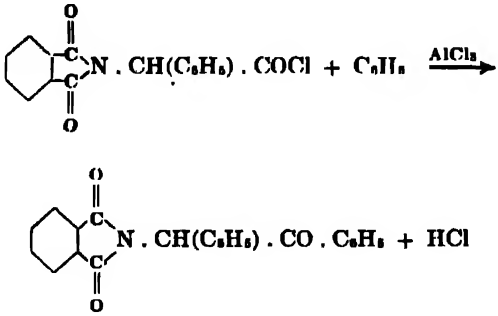
Upon acid hydrolysis, α-aminopropiophenone is secured.

Other phenones of phthalyl-ω-amino acid chlorides which have been similarly prepared include γ-phthalimidobutyrophenone,[250] α-phthal-imidoisobutyrophenone,[251] δ-phthalimidovalerophenone, and ε-phthal-imidocaprophenone.[252] A good yield of ζ-phthalimidooenantophenone, has been reported.[253]



[246] K. A. Böttcher, *Ber.*, 46, 3158-3167 (1913).
[247] S. Gabriel, *Ber.*, 42, 1249-1259 (1909).
[248] S. Gabriel, *Ber.*, 40, 2647-2650 (1907).
[249] S. Gabriel, *Ber.*, 41, 242-250 (1908).
[250] S. Gabriel and J. Colman, *Ber.*, 41, 513-521 (1908).
[251] S. Gabriel, *Ber.*, 44, 60 (1911).
[252] S. Gabriel and J. Colman, *Ber.*, 41, 2014-2017 (1908).
[253] S. Gabriel, *Ber.*, 42, 4050-4058 (1909).

Phthalylphenylglycyl chloride has been found to react in the same way, giving desylphthalimide (m.p. 157-158°) with benzene and aluminum chloride [254]:



α-Phalimido-*n*-butyryl chloride undergoes normal Friedel-Crafts condensation with benzene:

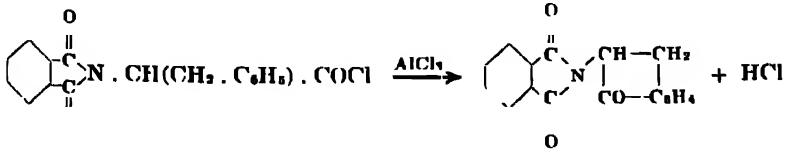
$$CH_3 . CH_2 . CH(N : O_2C_6H_4) . COCl + C_6H_6 \xrightarrow{AlCl_3}$$
$$CH_3 . CH_2 . CH(N : O_2C_6H_4) . COC_6H_5 + HCl$$

The phthalyl residue may be split off by hydrolysis to give α-aminobutyrophenone:

$$CH_3 . CH_2 . CH(N : O_2C_6H_4) . CO . C_6H_5 \xrightarrow{AlCl_3} CH_3 . CH_2 . CH(NH_2) . CO . C_6H_5$$

This affords a good method for the preparation of α-aminoaralkyl ketones.[255] The yield of α-phthalimidobutyrophenone, crystallized from 90 per cent alcohol, is 67 per cent.

However, the higher homolog, phthalimidohydrocinnamoyl chloride, does not give the expected ketone with benzene and aluminum chloride. There is formed instead β-phthalimido-α-hydrindone, m.p. 191°. This is obviously caused by the action of the catalyst on the acid chloride alone:



When carbamyl chloride is heated with benzene and aluminum chloride in carbon disulfide on a water-bath, benzamide is obtained in almost quantitative yield. According to Gattermann,[256] the reaction proceeds:

$$C_6H_6 + Cl . CO . NH_2 \xrightarrow{AlCl_3} C_6H_5 . CO . NH_2 + HCl$$

[254] E. Pfaehler, *Ber.*, **46**, 1700-1702 (1913).
[255] A. Hildesheimer, *Ber.*, **43**, 2796-2805 (1910).
[256] L. Gattermann and co-workers, *Ann.*, **244**, 29-76 (1888).

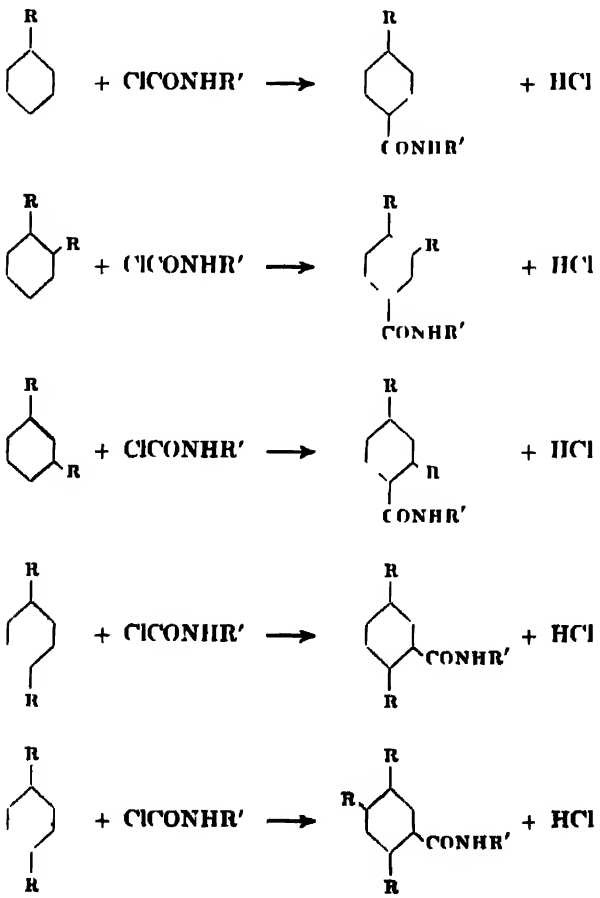
The reaction takes place analogously with N-alkyl carbamyl chlorides:

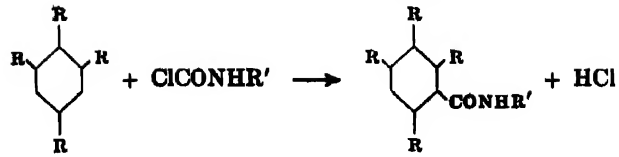
$$C_6H_6 + ClCONHC_2H_5 \longrightarrow C_6H_5CONHC_2H_5 + HCl$$

It is generally applicable to aromatic compounds. Gattermann prepared monoamides in the same way from the indicated hydrocarbons and carbamyl chlorides:

Hydrocarbon	Carbamyl Chloride
Toluene	carbamyl chloride
Toluene	N-methylcarbamyl chloride
Toluene	N-ethylcarbamyl chloride
Cumene	carbamyl chloride
o-Xylene	carbamyl chloride
m-Xylene	carbamyl chloride
p-Xylene	carbamyl chloride
Pseudocumene	carbamyl chloride
Durene	carbamyl chloride

In every case, para- or ortho- substitution was obtained, thus:





The reaction of phenyl isocyanate with aromatic hydrocarbons and aluminum chloride with formation of aromatic amides had been studied in 1885 by Leuckart.[257] Phenyl isocyanate, for example, reacts with benzene in the presence of aluminum chloride to give benzanilide. The condensation did not occur in the absence of aluminum chloride; Leuckart assumed that the reaction takes place in two phases. In the first step, phenyl isocyanate reacts with hydrochloric acid to form phenylcarbamyl chloride, and in the second step the acid chloride undergoes normal Friedel-Crafts condensation with formation of the anilide and evolution of hydrogen chloride:

(1) $C_6H_5NCO + HCl \longrightarrow ClCONHC_6H_5$

(2) $C_6H_6 + ClCONHC_6H_5 \longrightarrow C_6H_5CONHC_6H_5 + HCl$

This investigator reported that all true homologs of benzene reacted in a similar manner with phenyl isocyanate and aluminum chloride, the group $CONHC_6H_5$ usually taking the *para*- position. Gattermann's [258] application of carbamyl chloride to the reaction was an outgrowth of this study.

Since carbamyl chloride is produced by reaction of hydrogen chloride with a metal cyanate on cyanuric acid or on cyanic acid, a mention of methods in which these constituents have been used for the production of amides will be made here.

Gattermann and Rossolymo [258] found that a mixture of cyanic acid and hydrogen chloride in the presence of aluminum chloride acts in the same way as does carbamyl chloride on aromatic hydrocarbons. The reaction does not proceed as well with benzene as it does with benzene homologs, only a small amount of benzamide being obtained. Toluene, on the other hand, reacts more easily, giving *p*-toluamide, m.p. 158°. Ethylbenzene yields *p*-ethylbenzamide, m.p. 115-116°. From *m*-xylene is obtained 2,4-dimethylbenzamide, m.p. 178-179°.

The production of aromatic amides from potassium cyanate, hydrogen chloride, and an aromatic hydrocarbon has been patented. Thus, benzamide is obtained when a mixture of benzene, potassium cyanate and aluminum chloride is treated at atmospheric temperature with gaseous hydrogen chloride until potassium cyanate cannot be detected in the mixture.[259] *p*-Toluamide may be prepared similarly.

Aromatic hydrocarbons may be condensed with cyanoacetyl chloride in the presence of aluminum chloride to give the corresponding cyano-

[257] R. Leuckart, *Ber.*, **18**, 873-877 (1885); *J. Chem. Soc. Abs.*, **48**, 778 (1885).
[258] L. Gattermann and A. Rossolymo, *Ber.*, **23**, 1190-1199 (1890); *J. Chem. Soc. Abs.*, **58** (II), 974-975 (1890).
[259] German P. 584,142 (1933) to H. Hopff (to I. G. Farbenindustrie); *C. A.*, **28**, 174.

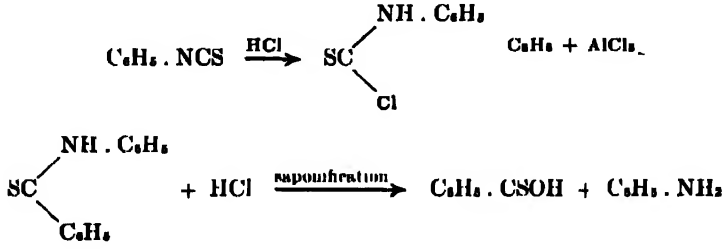
acetyl derivatives. The reaction, for example, with toluene, occurs according to the scheme:

$$C_6H_5CH_3 + NC.CH_2COCl \xrightarrow{AlCl_3} NC.CH_2CO.C_6H_4.CH_3 + HCl$$

The product from toluene melts at 104°. The reaction is claimed to be general for aromatic hydrocarbons.[260]

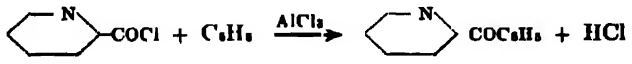
Aromatic thioanilides are formed by reaction of aryl isothiocyanates with aromatic hydrocarbons and aluminum chloride. The reaction takes place in two stages. Hydrogen chloride from the aluminum chloride combines with the isothiocyanate to form a thiocarbamyl chloride. This then reacts with the hydrocarbon to give the thioanilide. With homologs of benzene, the $CS.NHC_6H_5$ group goes *para*- to an alkyl group.[261]

Condensation of phenyl isothiocyanate with benzene and aluminum chloride, according to Gattermann, proceeds with formation of thiobenzanilide which, upon saponification, yields thiobenzoic acid:



Similar reaction with toluene gives thiotoluylanilide, $C_6H_5NH.CS.C_6H_4$-CH_3, m.p. 140-141°. *p*-Tolylisothiocyanate reacts as does the phenyl analog.[262]

In order to prepare ketones of the pyridine series, pyridine carboxylic acid chlorides, prepared by treatment of the acids with thionyl chloride, may be reacted with benzene in the presence of aluminum chloride:



In the case of the mono-carboxylic acids, reaction does not occur if the thionyl chloride used for the preparation of the acid chloride is quantitatively removed. With dicarboxylic acid chlorides, however, the reaction takes place even when the thionyl chloride is carefully removed.

The mono-ketones were produced by warming the acid chlorides with several parts of the aromatic hydrocarbon, if necessary in the presence of carbon disulfide as diluent, and then treating with somewhat more than the calculated amount of aluminum chloride in small portions. With the

[260] Brit. P. 342,373 (1929) to I. G. Farbenindustrie; *Brit. Chem. Abstracts-B*, 476 (1931).
[261] L. Gattermann, *J. prakt. Chem. (2)*, 59, 573-594 (1899); *J. Chem. Soc. Abstracts-76* (I) 694 (1899).
[262] A. Friedmann and L. Gattermann, *Ber.*, 25, 3525-3528 (1892); *J. Chem. Soc. Abs.*, 64 (I), 151 (1893).

dicarboxylic acid chlorides, however, it is best to prepare the aluminum-chloride complex first by gently warming the components and then adding the hydrocarbon.[263] In this way the following ketones were prepared:

α-pyridyl phenyl ketone
β-pyridyl phenyl ketone
β-pyridyl naphthyl ketone
α,β′-dibenzoyl pyridine
α,α′-dibenzoyl pyridine

Reaction of Benzene and Benzene Homologs with Acid Chlorides of Sulfur Compounds

Sulfuryl chloride acts on benzene with formation only of monochlorobenzene; but if aluminum chloride is added to the mixture, a considerable quantity of benzenesulfonyl chloride and a small amount of diphenyl sulfone are also obtained:

(1) $$C_6H_6 + SO_2Cl_2 \longrightarrow C_6H_5SO_2Cl + HCl$$

(2) $$2C_6H_6 + SO_2Cl_2 \longrightarrow C_6H_5SO_2C_6H_5 + 2HCl$$

Toluene is chlorinated by sulfuryl chloride both in the benzene nucleus and in the side chain, but in the presence of aluminum chloride, the chief product is *p*-toluenesulfonyl chloride, small quantities of *p*-chlorotoluene and *p*-ditolyl sulfone being also formed. *m*-Xylene and *p*-xylene behave in similar manner. Mesitylene is attacked by sulfuryl chloride at the ordinary temperature; if the mixture is kept cool, however, in the presence of aluminum chloride, chloromesitylene and mesitylsulfonyl chloride are formed.[264]

According to Böeseken,[265] dissociable chlorides like sulfuryl chloride act in the presence of aluminum chloride like mixtures of the non-dissociated molecule with activated chlorine atoms, and of their decomposition products. The catalyst displaces the equilibrium

$$SO_2Cl_2 \rightleftarrows SO_2 + Cl_2$$

considerably to the right.[266] Reaction products of the reacting aromatic hydrocarbon and the decomposition materials of sulfuryl chloride are to be expected. Thus benzene, sulfuryl chloride, and aluminum chloride gave much benzenesulfinic acid and chlorobenzene, but benzenesulfonyl chloride and diphenyl sulfone were also isolated. Toluene and sulfonyl chloride gave somewhat more toluene sulfonyl chloride than benzene, but much chloro-toluene and toluenesulfinic acid were likewise obtained in this case.

Since the products of the action of aluminum chloride on sulfonyl chloride vary with the temperature employed, the final Friedel-Crafts

[263] R. Wolffenstein and F. Hartwich, *Ber.*, **48**, 2043-2049 (1915).
[264] A. Tohl and O. Eberhard, *Ber.*, **26**, 2940-2945 (1893).
[265] J. Böeseken, *Rec. trav. chim.*, **30**, 381-391 (1911); *C. A.*, **6**, 623 (1912).
[266] *cf. O. Ruff, Ber.*, **35**, 4433-4470 (1902).

reaction products are necessarily manifold.[266] This is also true in reactions of pyrosulfuryl chloride and aluminum chloride with aromatic hydrocarbons. For example, toluene at −5° to 0°, with pyrosulfuryl chloride and aluminum chloride, gives toluene-*p*-sulfonic acid, *o*- and *p*-chlorotoluene, *p*-*p*′-ditolyl sulfone, and a substance (m.p. 215-217°) containing chlorine, but no sulfur.[267]

Thionyl chloride, though a common chlorinating agent, gives sulfoxides by reaction with aromatic compounds and aluminum chloride. Diphenyl sulfoxide (m.p. 70-71°) is readily prepared by the action of aluminum chloride on a mixture of benzene and thionyl chloride[268]:

$$2C_6H_6 + SOCl_2 \longrightarrow C_6H_5SOC_6H_5 + 2HCl$$

p,*p*′-bis(Bromophenyl)sulfoxide, $(p\text{-}BrC_6H_4)_2SO$, is prepared similarly.[269]

Since the reaction of sulfur dioxide with aromatic hydrocarbons and aluminum chloride with production of sulfinic acids probably involves intermediate formation of the compound $AlCl_2SO_2Cl$, reference is made to it at this time.[270] Knoevenagel and Kenner[271] have found that aromatic sulfinic acids can be readily prepared in a yield of about 80 per cent by the action of sulfur dioxide and aluminum chloride on aromatic hydrocarbons or their halogen derivatives at low temperature. They initiated the reaction by passing dry hydrogen chloride through the mixture and the resulting catalyst complex of aluminum chloride and aromatic sulfinic acid was decomposed by alkali. These workers prepared the sulfinic acids of the following hydrocarbons:

benzene
toluene
o-, *m*-, and *p*-xylene
mesitylene
pseudocumene
p-cymene

They also prepared sulfinic acids of *p*-chloro- and *p*-bromobenzene.

According to Smiles and Le Rossignol,[272] the action of sulfur dioxide on a mixture of an aromatic hydrocarbon and aluminum chloride takes place easily, even at 0°. The sulfur dioxide is rapidly absorbed, the reaction mixture becomes warm, and in a short time evolution of hydrogen chloride begins.

Hilbert and Johnson[273] modified Knoevenagel's method of preparing benzene sulfinic acid. They passed the sulfur dioxide into a mixture of benzene and aluminum chloride.

Phenyl mercaptans are formed by reducing sulfinic acids obtained by

[266] W. Steinkopf and K. Buchheim, *Ber.*, 54, 2063-2068 (1921).
[267] A. Schonberg, *Ber.*, 55, 2275 (1922).
[268] J. Böeseken, *Rec. trav. chim.*, 29, 315-339 (1910); *C. A.*, 5, 678.
[269] C. Friedel and J. M. Crafts, *Bull. soc. chim.*, 30, 1 (1878); *Compt. rend.*, 86, 1368-1371 (1878); A. Adrianovsky, *Ber.*, 12, 853 (1879); *Bull. soc. chim.*, 31, 495-498 (1879).
[270] E. Knoevenagel and J. Kenner, *Ber.*, 41, 3315-3322 (1908).
[271] S. Smiles and R. Le Rossignol, *J. Chem. Soc.*, 93, 745-763 (1908).
[272] G. E. Hilbert and T. B. Johnson, *J. Am. Chem. Soc.*, 51, 1526-1536 (1929).

interaction of benzene or benzene homologs with sulfur dioxide and aluminum chloride.[274]

p-Fluorobenzenesulfinic acid has been prepared by reaction of fluorobenzene with sulfur dioxide, hydrogen chloride, and aluminum chloride in carbon disulfide.[275]

The reaction of thiophosgene with benzene and aluminum chloride has been reported to give thiobenzophenone[276]; but since the ketone decomposed upon distillation, it was not isolated even *in vacuo*. By treatment of the product with phenylhydrazine and hydroxylamine, however, it was ascertained that thiobenzophenone had been obtained.

The reaction of benzenesulfonyl chloride or its derivatives with aromatic hydrocarbons,

$$RSO_2Cl + HR' \xrightarrow{AlCl_3} RSO_2R' + HCl$$

is similar to the analogous reaction of benzoyl chloride

$$RCOCl + HR' \xrightarrow{AlCl_3} RCOR' + HCl$$

Thus by treating benzenesulfonyl chloride with benzene and anhydrous aluminum chloride, Beckurts and Otto[277] obtained diphenyl sulfone, $C_6H_5SO_2C_6H_5$. It has been shown that benzene sulfonyl chloride yields in carbon disulfide with 1 mole of aluminum chloride the complex, $C_6H_5SO_2Cl + AlCl_3$, which upon addition of 1 mole of benzene in carbon disulfide, gives the diphenyl sulfone-aluminum chloride complex.[278] The velocity of the reaction of benzenesulfonyl chloride with benzene or with chlorobenzene in the presence of anhydrous aluminum chloride at 30° has been studied by Olivier.[279]

Benzenesulfonyl chloride with chlorobenzene in the presence of anhydrous aluminum chloride yields *p*-chlorophenyl phenylsulfone.[280] In the same way, toluene and benzenesulfonyl chloride gave phenyl *p*-tolyl sulfone.[277]

An extended study of the mechanism of Friedel-Crafts reactions was made by Olivier, using *p*-bromobenzenesulfonyl chloride and benzene. He found that the acid chloride combined with aluminum chloride to form an active compound, $Br.C_6H_4SO_2Cl.AlCl_3$. He suggested that the aluminum chloride does not combine with benzene but activates the benzene, whether combined with the sulfonyl chloride or the sulfone.[281] Reaction in carbon disulfide indicated an autocatalytic action of benzene on the formation of the complex; hydrogen chloride had no influence in

[274] U. S. P. 1,993,863 (1935) to E. Havas (to du Pont); *C. A.*, **29**, 2548
[275] R. M. Hann, *J. Am. Chem. Soc.*, **57**, 2166-2167 (1935).
[276] H. Bergreen, *Ber.*, **21**, 337-352 (1888).
[277] H. Beckurts and R. Otto, *Ber.*, **11**, 2066-2070 (1878).
[278] J. Böeseken, *Rec. trav. chim.*, **19**, 24-25 (1900).
[279] S. C. J. Olivier, *Rec. trav. chim.*, **33**, 244-251 (1914); *J. Chem. Soc. Abs.*, **106** (II), 846 (1914).
[280] Haahl, *Compt. rend.*, **177**, 194-195 (1923); *J. Chem. Soc. Abs.*, **124** (I), 909 (1923); *cf.* Beckurts and Otto, *loc. cit.*
[281] S. C. J. Olivier and J. Böeseken, *Verslag Akad. Wetenschappen*, **21**, 979-988; *C. A.*, **8**, 1424 (1914).

this effect.[282] An excess of benzene formed *p*-bromophenyl phenyl sulfone. The main reaction postulated involved $4\text{-}BrC_6H_4SO_2Cl.AlCl_3 + C_6H_6 \longrightarrow 4\text{-}BrC_6H_4SO_2AlCl_2 + C_6H_5Cl + HCl$, but chlorobenzene could not be isolated and $BrC_6H_4SO_2.AlCl_3$ in an impure form was obtained only from very concentrated solutions. Since the sulfone is not converted to sulfinic acid by aluminum chloride, it was concluded that sulfinic acid obtained in carbon disulfide solution came from a small amount of sulfur monochloride formed during the reaction.

Velocity of reaction experiments indicated that an excess of benzene accelerated the dissociation reaction, whereas an excess of the sulfonyl chloride retarded reaction. Benzene and toluene were found to be accelerating agents; chlorobenzene, bromobenzene, and nitrobenzene were retarders. An attempt to find a non-reactive solvent showed that many compounds formed complexes with aluminum chloride. The reaction was shown to be monomolecular with respect to $BrC_6H_4SO_2Cl.AlCl_3$, the velocity varying with the quantity of aluminum chloride employed Olivier concluded [282]

(1) that *p*-bromobenzenesulfonyl chloride reacts only when combined with aluminum chloride;
(2) the product, $BrC_6H_4SO_2C_6H_5$, also forms a complex with aluminum chloride;
(3) the velocity of reaction is proportional to aluminum chloride if the latter is not in excess;
(4) aluminum chloride in excess causes a high increase in reaction velocity.

Replacing the bromine with other substituents in this same reaction indicated that the substituents influenced the velocity of reaction. The substituents CH_3, H, I, Br, Cl, and NO_2 (in the *meta*- position) showed reaction velocities diminishing in the above order. The influence seemed the same whether the substituent was in the nucleus of the acid chloride or of the hydrocarbon to be substituted, except that in the latter case a greater influence was shown.[283] As a matter of fact, the presence of a nitro group in the hydrocarbon to be substituted inhibits reaction in most cases. It was also believed that the catalytic action of the aluminum chloride came partly from that combined with the sulfonyl chloride and partly from that combined with the sulfone; however, an excess of free aluminum chloride indicated that the latter was a stronger catalyst than the combined aluminum chloride.[284]

Olivier [285] later investigated the apparent inactivation or "paralysis" of the aluminum chloride when combined either with *p*-bromosulfonyl chloride or diphenyl sulfone. Other sulfone complexes showed an almost identical degree of paralysis of the aluminum chloride. The varying reac-

[282] S. C. J. Olivier, *Rec. trav. chim.*, 33, 91-132 (1913); *C. A.*, 8, 2013.
[283] S. C. J. Olivier, *Rec. trav. chim.*, 33, 244-251 (1914); *J. Chem. Soc. Abs.*, 106 (II), 846 (1914)
[284] S. C. J. Olivier, *Chem. Weekblad*, 11, 372-377 (1914), *J. Chem. Soc. Abs.*, 106 (I), 676 (1914) *C. A.*, 10, 196.
[285] S. C. J. Olivier, *Rec. trav. chim.*, 35, 109-122 (1915); *C. A.*, 10, 1635

tion velocities previously noted were attributed to the varying substituents in the benzene nucleus rather than to the degree of inactivation of aluminum chloride. These complexes show only 1/200 of the activity of free aluminum chloride. In mixed sulfone solutions the aluminum chloride combined in a larger proportion with that sulfone which showed the greatest reaction velocity with benzene. Hence, the more readily an addition compound is formed the more active it is with respect to benzene.

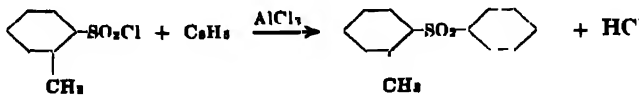
Olivier [286] also studied the formation of sulfones in a solvent other than the aromatic hydrocarbon itself, for example, in benzenesulfonyl chloride. The reaction was conducted by dissolving aluminum chloride in excess benzenesulfonyl chloride and adding the hydrocarbon. It was observed that one mole of aluminum chloride could transform only one mole of benzenesulfonyl chloride, which was in agreement with the results obtained in benzene solution. To explain the results obtained on velocity measurements, the author suggested that the complex, $C_6H_5SO_2Cl.AlCl_3$, existed in dilute solution, but that in a more concentrated solution or upon the addition of benzene or chlorobenzene, association to $(C_6H_5SO_2Cl.AlCl_3)_x$ occurred. The suggestion was confirmed by molecular weight determinations in benzene; but since chlorobenzene was shown to have no association effect, this hypothesis was untenable. Olivier considered that ternary addition compounds of the sulfones were probably not formed. The Friedel and Crafts synthesis of sulfones has also been studied by Prins.[287]

Groves and Turner [288] report the reaction of *p*-chlorobenzenesulfonyl chloride with bromobenzene and aluminum chloride to give *p*-chlorophenyl *p*-bromophenyl sulfone, m.p. 157°.

According to Böeseken,[289] *p*-chlorobenzenesulfonyl chloride begins to be decomposed at 190°, giving sulfur dioxide and dichlorobenzene at first, followed by evolution of hydrogen chloride and tarring.

p-Iodobenzenesulfonyl chloride has been condensed with benzene in the presence of anhydrous aluminum chloride to give the expected product, *p*-iodophenyl phenyl sulfone, m.p. 141°.[290]

o-Toluenesulfonyl chloride has been treated [291] with benzene and aluminum chloride to give a 95 per cent yield of *o*-tolyl phenyl sulfone:

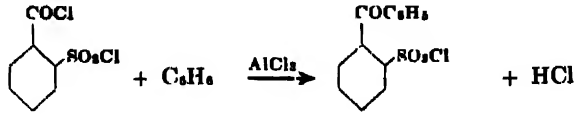


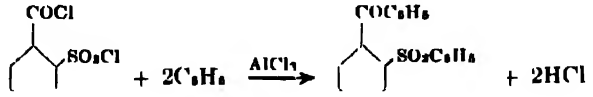
In the same way from *p*-nitrosulfonyl chloride and toluene there was obtained an 85 per cent yield of *p*-nitrophenyl *o*-tolyl sulfone, m.p. 159°.

The dichloride of *o*-sulfobenzoic acid reacts with aromatic hydro-

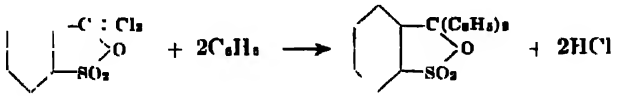
[286] S. C. J. Olivier, *Rec. trav. chim.*, 35, 166-178 (1915); *C. A.*, 10, 1853.
[287] H. J. Prins, *Chem. Weekblad*, 11, 418 (1914).
[288] J. G. Groves and E. E. Turner, *J. Chem. Soc.*, 509-511 (1929).
[289] J. Boeseken, *Rec. trav. chim.*, 32, 1-14; *C. A.*, 11, 1702 (1913).
[290] C. Willgerodt and M. Klinger, *J. prakt. Chem.*, 85, 189-198 (1912); *C. A.*, 6, 2400.
[291] F. Ullmann and A. Lehner, *Ber.*, 38, 729-742 (1905).

carbons to give mono- or di-substitution products, depending on the amount of hydrocarbon employed.[292]

(I) 

(II) 

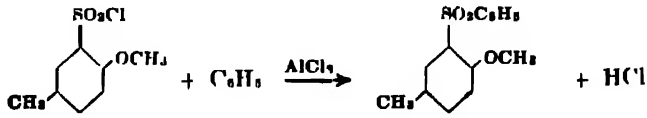
The tautomeric chloride has been reported to react as a lactone;[293]



but according to Cobb,[294] the lactone structure of the resulting product has not been definitely established.

The reaction of benzenesulfonyl fluoride or its derivatives with benzene and aluminum chloride yields diphenyl sulfones in good yields.[295]

Alkoxy-substituted benzenesulfonyl chlorides undergo normal reaction with benzene and aluminum chloride. Thus Heppenstall and Smiles[296] report that 2-methoxy-5-methylbenzenesulfonyl chloride and benzene yield 6-methoxy-*m*-tolyl phenyl sulfone, m.p. 140°:



Chlorine in the ring likewise does not affect the course of the reaction, 5-chloro-2-methoxybenzenesulfonyl chloride with benzene giving the expected 5-chloro-2-methoxyphenyl phenyl sulfone, m.p. 144°.

The use of methylsulfonyl chloride and ethylsulfonyl chloride in the Friedel-Crafts reaction has been investigated.[297] At high temperatures in the presence of aluminum chloride methylsulfonyl chloride is decomposed quantitatively into sulfur dioxide and methyl chloride. Ethylsulfonyl chloride under like conditions gives not only sulfur dioxide and ethyl chloride, but also hydrogen chloride and tar. The sulfonyl chloride

[292] I. Remsen and A. P. Saunders, *Am. Chem. J.*, 17, 347-368 (1895); *J. Chem. Soc. Abs.*, 68 (I) 474 (1895).
[293] R. List and M. Stein, *Ber.*, 31, 1668-1672 (1898).
[294] Cobb, *Am. Chem. J.*, 35, 486-508 (1906).
[295] W. Steinkopf, *J. prakt. Chem.*, 117, 1-82 (1927); *C. A.*, 21, 3603.
[296] M. E. Heppenstall and S. Smiles, *J. Chem. Soc.*, 899-905 (1928).
[297] J. Bieneken and H. W. Van Ockenburg, *Rec. trav. chim.*, 33, 317-323 (1914); *C. A.*, 9, 1313

obviously decomposes to give hydrogen chloride, sulfur dioxide, and ethylene.

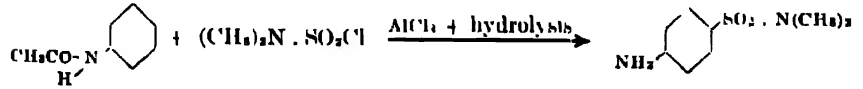
At low temperatures, aluminum chloride forms addition compounds with the alkylsulfonyl chlorides. These addition compounds react with benzene to give sulfones:

$$CH_3SO_2Cl.AlCl_3 + C_6H_6 \longrightarrow CH_3SO_2C_6H_5.AlCl_3 + HCl$$

It was assumed that in the reaction of alkylsulfonyl chlorides with benzene, aluminum chloride had three functions:

1. A dislocating function; it dislocates the active chlorine of the acid chloride, and the active hydrogen of the benzene so that condensation occurs.
2. An associating function. This is observed at low temperatures. Thus formation of the acid chloride-aluminum chloride additive compound is effected.
3. A dissociating function, apparent at higher temperatures. This effects decomposition of the acid chloride.

Reaction with Acetanilide.—The preparation of aromatic amines containing a sulfonamide group in the aromatic ring has been claimed by interaction of an acyl- or arylsulfonyl derivative of an aromatic amine and a dialkylaminosulfonyl halide at 20-100° in the presence of aluminum chloride.[298] Thus, acetanilide with dimethylsulfamyl chloride and aluminum chloride gives, after steam distillation, *p*-aminobenzenesulfonyldimethylamide:



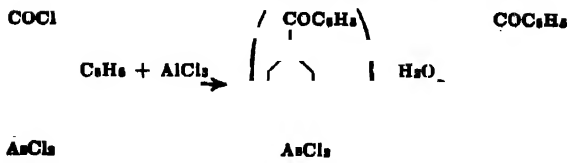
Acid Chlorides of Arsenic, Selenium, and Phosphorus

Although the Friedel-Crafts reaction has found little application in synthesis of metallo-organic compounds, the condensation of arsino- or seleno-benzoyl chlorides with aromatic compounds and aluminum chloride with production of ketones has been reported. Phosphoryl chloride has been condensed with aromatic hydroxy- compounds and aluminum chloride to give esters.

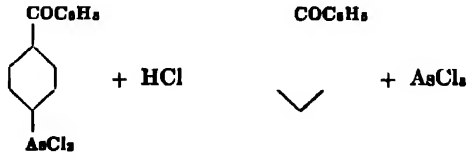
Arsenated benzoyl chloride enters into the Friedel-Crafts reaction, condensing easily with aromatic hydrocarbons and phenyl ethers in the presence of aluminum chloride to give arsino-aryl ketones.[299] Dichloro-*p*-arsinobenzoyl chloride with benzene and aluminum chloride in carbon disulfide solution yields benzophenone-*p*-arsenious oxide, probably according to the scheme:

[298] British P. 505,812 (1939) to Chinoin Gyogyszer es Vegyeszeti Termekek Gyara R. T. (Keresaty and Wulf); *Brit. Chem. Abstracts*-B, 885 (1939).

[299] W. L. Lewis and H. C. Cheetham, *J. Am. Chem. Soc.*, 43, 2117-2121 (1921).



When the reaction is too vigorous, the arsenic is freed:

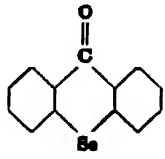


However, the amount of benzophenone formed does not exceed 10 per cent, usually being about 0.5-1 per cent, whereas the yield of the arsenated benzophenone is 50-60 per cent. Toluene reacts similarly.

Condensation of dichloro-*p*-arsinobenzoyl chloride with phenyl ethers under like conditions proceeds very smoothly. Since the substituted arsenious oxides were found difficult to isolate, they were oxidized to the corresponding arsonic acids and recovered as such. Anisole, phenetole, and diphenyl ether thus gave 4-methoxy-, 4-ethoxy-, and 4-phenoxybenzophenone-4'-arsonic acids, respectively in 60-70, 55, and 50 per cent yields.

The Friedel-Crafts reaction was similarly extended to like condensations with dichloro-*o*-arsinobenzoyl chloride.[300]

Selenium acid halides may be used as acylating agents in Friedel-Crafts ketone synthesis. *o*-Chloro-selenobenzoyl chloride with benzene and aluminum chloride produces selenoxanthone,



and toluene gives methylselenoxanthone in a similar manner.[301]

Phosphoryl chloride condenses with aromatic or heterocyclic compounds in the presence of aluminum chloride to yield the corresponding phosphates.[302] Use of less than three moles of the aromatic component to one mole of phosphoryl chloride results in the formation of mono- or

[300] W. L. Lewis and H. C. Chretham, *J. Am. Chem. Soc.*, 45, 510-515 (1923).
[301] R. Lesser and R. Weiss, *Ber.*, 57, 1077-1082 (1924).
[302] German P. 367,954 to E. Tschunkur and E. Knieper: *C. Z.*, 1923 (II), 915-916; British P 455,014 (1936) to Celluloid Corp., *C. A.*, 31, 1427.

di-halogenated phosphates.[303] A halogenated phenol or a mixture of phenols may be used;[304] however, the above reactions go without aluminum chloride.

Polynuclear Hydrocarbons and Aliphatic Acid Chlorides

In 1886, Pampel and Schmidt[305] reacted naphthalene dissolved in petroleum ether with acetyl chloride in the presence of aluminum chloride and obtained naphthyl methyl ketone, boiling at 296-299°. They used approximately equal amounts by weight of the reactants and catalyst. A few months later, Claus and Feist[306] used carbon disulfide as the solvent and obtained what they considered to be only the α-naphthyl methyl ketone, b.p. 295-297°. However, in 1897, Rousset[307] reported that by the addition of an equivalent of the acid chloride in small quantities to a boiling solution of naphthalene in carbon disulfide with aluminum chloride, a mixture of the α- and β-substituted naphthalenes were obtained. He secured fair yields of ketones from naphthalene and acid chlorides up to butyryl chloride.

That the yields of the ketones obtained were small may be seen by the fact that in 1911 Stobbe and Lenzner[308] described an improved method for the preparation of α- and β-naphthyl methyl ketone, based on that of Raeder,[309] in which the total yield of both ketones was 30 per cent based on the acetyl chloride. Here, instead of using equivalent amounts of the reactants, there were used 1 mol of acetyl chloride, 2 mols of aluminum chloride, and 2 mols of naphthalene at 15°. The yields obtained here were said to be even better than those which could be obtained by the method used by Perrier,[310] who had reported that good yields of aralkyl ketones could be obtained by first preparing a complex of the acyl chloride and aluminum chloride in carbon disulfide and then treating this complex with the hydrocarbon.

Caille[311] used low temperatures (0°) and carbon disulfide as the solvent and reported yields of from 60-80 per cent of α-naphthyl derivatives.

However, much later, Samuelsson[312] stated that, regardless of the temperature of preparation (0-50°), in no case was the product the pure α-compound. He obtained naphthyl methyl ketones in 75 per cent yield, but only 50-70 per cent of the substance consisted of the α-isomeride. When the reaction took place with aluminum chloride in nitrobenzene, however, the pure β-form was obtained. Pictet and Manevitch[313] report that by addition of aluminum chloride to a solution of naphthalene and

[303] U. S. P. 2,117,290-1 (1938) to E. C. Britton and S. L. Bass (to Dow Chemical Co.); British P 497,174 to Dow Chemical Co.
[304] U. S. P. 2,033,016 (1936) to S. L. Bass (to Dow Chemical Co.), *C. A.*, 29, 91; U. S. P. 2,033,018 (1936) to E. C. Britton (to Dow Chemical Co), *C. A.*, 30, 2988.
[305] O. Pampel and G. Schmidt, *Ber.*, 19, 2896-2899 (1886).
[306] Ad. Claus and P. Feist, *Ber.*, 19, 3180-3182 (1886).
[307] L. Rousset, *Bull. soc. chim. (3)*, 15, 58-72 (1896); *J. Chem. Soc. Abs.*, 72 (I), 75 (1897).
[308] H. Stobbe and A. Lenzner, *Ann.*, 380, 93-99 (1911).
[309] H. Raeder, Diss., Leipsig, 15 (1902).
[310] G. Perrier, *Ber.*, 33, 815-816 (1900).
[311] E. Caille, *Compt. rend.*, 153, 393-394 (1911); *J. Chem. Soc. Abs.*, 100 (I), 792 (1911).
[312] E. Samuelsson, *Svensk. Kem. Tidskr.*, 34, 7-9 (1922); *J. Chem. Soc. Abs.*, 122 (I), 823 (1922).
[313] A. Pictet and B. Manevitch, *Arch. Sci. phys. nat. (4)*, 35, 40-47 (1913); *J. Chem. Soc. Abs.*, 104 (I), 298 (1913).

acetyl chloride in carbon disulfide, a mixture of α- and β-naphthyl methyl ketones is obtained.

The influence of different solvents on the formation of isomers of naphthyl methyl ketone was studied by Chopin.[314] With petroleum ether, the α- and β-isomers were formed in nearly equal quantities. The β-isomer was found to be chiefly formed in nitrobenzene, and the α-isomer chiefly in bromobenzene. The α-isomer was found to be formed exclusively in chlorobenzene and carbon disulfide.

St. Pfau and Ofner[315] also studied the influence of the solvent on the formation of methyl naphthyl ketone and found that the position taken by the substituent is determined by the solvent used. He, too, found that in petroleum ether equal proportions of α- and β-compounds were produced. In chlorobenzene, 42 per cent of the α- and 58 per cent of the β-isomer were formed; whereas in carbon disulfide 65 and 89 per cent, respectively, were obtained. Nitrobenzene as the solvent gave 11 per cent of the α- and 89 per cent of the β-ketone.

Rivkin[316] reviewed the reaction, and pointed out that Chopin neglected the factor of mechanical agitation, which is necessary for the production of uniformly high yields. In nitrobenzene, the β-isomer is formed predominantly; whereas in benzene a mixture of the α- and β-isomers in equivalent proportion is secured. The formation of colored by-products when nitrobenzene was used was avoided by working below 10°. The formation of resinous materials was also reduced by adding aluminum chloride into the mixture of the reactants in the solvent, instead of adding the acetyl chloride to a mixture of aluminum chloride with the naphthalene and the solvent. The optimum temperature was found to be 10°.

The following conditions and proportion of reactants were used in experiments using (1) benzene and (2) nitrobenzene as the solvents.

	(1)	(2)
Naphthalene	130 g	130 g
Acetyl chloride	80 g	83 g
Solvent	1000 g	500 g
Aluminum chloride	150 g	150 g
Reaction time	6 hrs	9 hrs, 20 min
Yield	69.5 g	154 g

Since the use of benzene as solvent results in the formation of both α- and β-isomers, in experiment (1) the product was an equal mixture of the α- and β-naphthyl methyl ketone. In experiment (2) the product was β-naphthyl methyl ketone, the 154 g noted above being the weight of the β-isomer obtained after filtration from traces of the α-isomer.

Levy[317] reported the use of temperatures of −5° to 0° in the preparation of β-naphthyl methyl ketone. He, too, added aluminum chloride to a mixture of naphthalene and acetyl chloride in nitrobenzene.

[314] M. Chopin, *Bull. soc. chim.*, 35, 610-614 (1924); *C. A.*, 18, 2689.
[315] A. St. Pfau and A. Ofner, *Helv. Chim. Acta*, 9, 669-671 (1926); *C. A.*, 21, 404.
[316] S. M. Rivkin, *J. Gen. Chem. (U.S.S.R.)*, 5, 277-280 (1935); *C. A.*, 29, 5102.
474 (1936).
[317] G. Levy, *Ann. chem. XI*, 9, 5-87 (1938); *Brit. Chem. Abstracts-A*, II, 89-90 (1938).

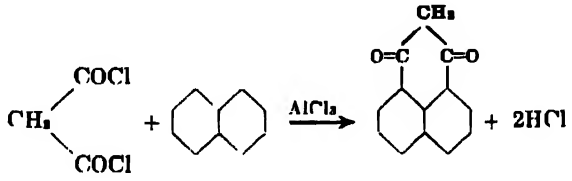
Low temperatures (0°) were used in the preparation of heptadecyl α-naphthyl ketone (m.p. 54.5-56°) by adding aluminum chloride to a mixture of stearyl chloride and naphthalene in carbon disulfide.[318] A similar reaction of stearoyl chloride with tetralin leads to the production of heptadecyl tetrahydronaphthyl ketone, m.p. 49.5-50°.

According to an I. G. patent,[319] chloroacetyl chloride reacts with naphthalene to yield a diketone. A sufficient quantity of the acid chloride must be used to allow double substitution.

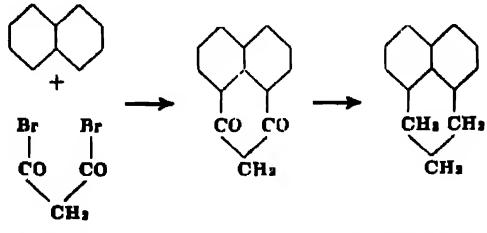
The reaction of β-chloropropionyl chloride or of β-chloro-*n*-butyryl chloride on naphthalene, α-chloro, α-bromo-, and 1,6-dimethylnaphthalene has been studied by Mayer and Müller.[320]

Aluminum chloride decomposes oxalyl chloride into carbon monoxide and phosgene more rapidly than it catalyzes the Friedel-Crafts reaction of oxalyl chloride with naphthalene. Reaction, therefore, results in the production of a mixture of α-naphthoic acid (m.p. 160°) and β-naphthoic acid (m.p. 182°). The carboxyl group is introduced by the phosgene.[321]

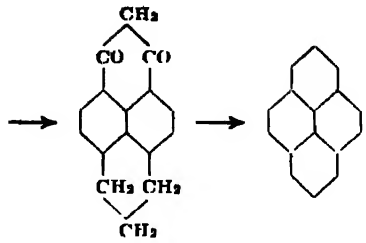
With malonyl chloride, naphthalene condenses in the presence of aluminum chloride to give *peri*-naphthindandione [322]:



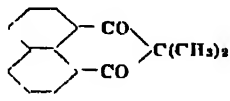
The condensation of naphthalene with malonyl bromide in the presence of aluminum chloride may be used for the preparation of pyrene.[323] The first product, *peri*-naphthindandione, is reduced with concentrated hydriodic acid under pressure; the resulting superhydrogenated material is led over metallic copper, whereby *peri*-naphthindan is formed. This is then condensed with more malonyl bromide to yield 1,2,3,4,5,6-hexahydro-1,3-diketopyrene, which may be reduced by distilling with zinc dust to pyrene. The scheme is:



[318] L. A. Mikeska, C. F. Smith, and E. Lieber, *J. Org. Chem.*, 2, 499-505 (1938).
[319] German P. 576,253 (1933) to I. G. Farbenindustrie; *C. A.*, 27, 3722; *Chem. Zentr.*, 1933, II, 619.
[320] F. Mayer and P. Müller, *Ber.*, 60, 2278-2283 (1927).
[321] C. Liebermann and M. Zsuffa, *Ber.*, 44, 202-210 (1911).
[322] German P. 283,865 (1915) to Badische Anilin und Soda Fabrik, *Chem. Zentr.*, 1915, *I*, 965.
[323] K. Fleischer and E. Retze, *Ber.*, 55, 3280 (1922).

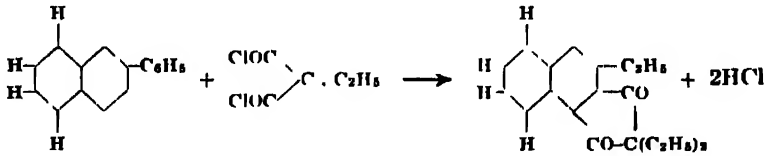


Dimethylmalonyl chloride and naphthalene react to give three isomeric products: 1,8-naphthodimethylindandione,



m.p. 101°; 1,2-naphthodimethylindandione, m.p. 120-121°; and 2,3-naphthodimethylindandione, m.p. 137-137.5°.[324] Diethylmalonyl chloride reacts similarly with naphthalene, three analogous isomeric products being formed.[325]

In the condensation of a penta-substituted naphthalene like 2-ethyl-5,6,7,8,tetrahydronaphthalene with diethylmalonyl chloride there is, of course, only one isomer possible, since only the 3- and 4-positions are available:



The 2,2,4-triethyltetrahydro-α-β-indane-1,3-dione thus formed melts at 39°.[326]

β-Methylnaphthalene has been reacted with acetyl chloride by Dziewonski and Brand.[327] To 100 g of β-methylnaphthalene and 100 g of acetyl chloride in 600 cc of carbon disulfide was added 50 g of aluminum chloride; the mixture was heated to boiling, and 80 g of aluminum chloride were added in portions. After heating for about two hours, it was left for twelve hours. Upon addition of dilute HCl and removal of the carbon disulfide, the residue was fractionated *in vacuo*. One fraction, b_{14} 176-180°, contained 2-methyl-6-acetylnaphthalene (m.p. 70-71°) and 2-methyl-8-acetylnaphthalene. Fraction B, b_{14} 215-220°, contained 2-methyl-6,8-diacetylnaphthalene (m.p. 127-128°).

[324] M. Freund and K. Fleischer, *Ann.*, **399**, 182-241 (1913); *C. A.*, **7**, 3737.
[325] M. Freund and K. Fleischer, *Ann.*, **373**, 291-336 (1910); *J. Chem. Soc. Abs.*, **98** (I), 490 (1910); *Ann.*, **402**, 51-76 (1913); *J. Chem. Soc. Abs.*, **106** (I), 48 (1914).
[326] K. Fleischer and E. Retse, *Ber.*, **56**, 228-234 (1923); *J. Chem. Soc. Abs.*, **124** (I), 231 (1923).
[327] K. Dziewonski and M. Brand, *Roczniki Chem.*, **12**, 693-701; *Bull. intern. acad. polon. sci., Classe sci. math. nat.*, 1933 A, 99-107 (in German); *C. A.*, **27**, 4533.

According to Kon and Weller [328] the condensation of β-methylnaphthalene with acetyl chloride in nitrobenzene solution constitutes a good method of preparation of 6-acetyl-2-methylnaphthalene because only a very small amount of the 2,8-isomer is formed.

α-Methylnaphthalene in nitrobenzene with acetyl chloride and aluminum chloride at −3° to −1° and then at room temperature for 24 hours gives 4-acetyl-1-methylnaphthalene, m.p. 41°.[329] Similar treatment of 2,6-methylnaphthalene with acetyl chloride gave 2,6-dimethyl-1-acetylnaphthalene (m.p. 71°) in 80 per cent yield. The product obtained by using propionyl chloride was the expected 2,6-dimethyl-1-propionylnaphthalene (m.p. 49°) in 60 per cent yield.[330]

The acetylation of α- and β-brominated naphthalenes has been reported by Schweitzer,[331] who obtained acetyl-α-bromonaphthalene (b.p. 345-347°) by the action of acetyl chloride on α-bromonaphthalene in the presence of aluminum chloride in carbon disulfide in the cold. Condensation with β-bromonaphthalene was also reported to take place in the cold; better results were obtained, however, by heating the mixture. The product, an acetyl-β-naphthalene, melted at 102°.

The acetylation was performed more recently by Dziewonski and Sternbach.[332] The product obtained from α-bromonaphthalene was found to be 1-bromo-4-acetylnaphthalene (b.p. 193-196°/18 mm), and that from β-bromonaphthalene was identified as 2-bromo-1-acetylnaphthalene, m.p. 64-65°. Schweitzer [331] was unable to secure an acetylation product from 1,4-dibromonaphthalene.

The chloride of 4-methylhydrindene-4-carboxylic acid and α-chloronaphthalene in tetrachloroethane with aluminum chloride gives a condensation product, probably 2-chloro-7-methyl-5,6-cyclopenteno-1,9-benzanthr-10-one, m.p. 215°. α-Chloronaphthalene is partly isomerized to the β-isomer by aluminum chloride in tetrachloroethane at room temperature.[333]

According to Barbot,[334] the Friedel-Crafts reaction of tetralin results exclusively in substitution in the β-position. Acetyl chloride with tetralin and aluminum chloride in carbon disulfide solution gave a 90 per cent yield of methyl β-tetrahydronaphthyl ketone.[335] Barbot similarly reacted propionyl-, butyryl-, and isobutyryl chlorides with tetralin. More recently, Fernholz and his co-workers [330] reacted higher acid chlorides with tetralin. The acid chloride from 15 g of the corresponding acid was decanted into 100 cc of carbon disulfide containing 8 g of tetralin. Then 8 g of aluminum chloride was gradually added, and the mixture was

[328] G. A. R. Kon and W. T. Weller, *J. Chem. Soc.*, 792-794 (1930).
[329] K. Dziewonski and M. Marusinska, *Bull. acad. polonaise*, 1938 A, 316-323; *Brit. Chem. Abstracts-A* (II), 23 (1939).
[330] K. Dziewonski, K. Stec, and P. Zagala, *Bull. intern. acad. polon. sci. Classe sci. math. nat.*, 1938 A, 324-330 (in German); *C. A.*, 33, 1713.
[331] R. Schweitzer, *Ber.*, 24, 550-552 (1891); *J. Chem. Soc. Abs.*, 60 (I), 684 (1891).
[332] K. Dziekonski and L. Sternbach, *Bull. acad. polonaise*, A, 59-68 (1931); *Brit. Chem. Abstracts-A*, 1156 (1931).
[333] L. F. Fieser and F. Desreux, *J. Am. Chem. Soc.*, 60, 2255-2262 (1938).
[334] A. Barbot, *Bull. soc. chim. (4)*, 47, 1314-1323 (1930); *C. A.*, 25, 943; *C. Z.*, 1931, I, 939.
[335] *cf. W. Scharwin, Ber.*, 35, 2511-2515 (1902).
[330] E. Fernholz, S. Ansbacher and H. B. MacPhillamy, *J. Am. Chem. Soc.*, 62, 430-432 (1940).

allowed to stand over night. The following ketones were obtained from Tetralin or from 2-methyl-5,6,7,8-Tetralin and the appropriate acid chloride:

-5,6,7,8-tetrahydronaphthylketone	% yield
2-*n*-pentadecyl	56
2-*n*-hexadecyl	63 (on hydrocarbon)
methyl-3-*n*-heptadecyl	

In reacting 2-methyl-5,6,7,8-tetralin with acetyl chloride, substitution takes place in the 3-position, the product being 3-acetyl-2-methyl-5,6,7,8-tetrahydronaphthalene.[337]

Oxalyl chloride with tetrahydronaphthalene in the presence of aluminum chloride gives a 70 per cent yield of β-tetrahydronaphthalene carboxylic acid, by carboxylation of the hydrocarbon through the phosgene evolved by the action of aluminum chloride on oxalyl chloride. The production here of only the β-isomer is remarkable in that reaction of oxalyl chloride with naphthalene yields both α- and β-naphthoic acids.[338]

The reaction of tetrahydronaphthalene with substituted malonyl chlorides has been studied by Fleischer and Seifert [339] and by von Braun and co-workers.[338]

1-Benzylnaphthalene and acetyl chloride in the presence of aluminum chloride in carbon disulfide at the ordinary temperature was reported by Dziewonski and Moszew [340] to give 4-acetyl-1-benzylnaphthalene, m.p. 75°. According to an I. G. patent [341] 4-acetyl-1-benzylnaphthalene thus obtained melts at 78°.

2-Benzylnaphthalene was similarly reacted with acetyl chloride by Dziewonski and Wodelski.[342] They obtained 6-acetyl-2-benzylnaphthalene, m.p. 96°.

Naphthalene and Aroyl Chlorides

The condensation of naphthalene with benzoyl chloride in the presence of aluminum chloride was reported by Roux [343] and Rospendowski [344] to result in the production of 1-benzoylnaphthalene (m.p. 75.5-76°) and 2-benzoylnaphthalene, m.p. 82°. Elbs [345] obtained the same ketones. Montagne [346] reported that the interaction of benzoyl chloride and naphthalene in carbon disulfide with aluminum chloride yields 78.5 per cent of 1-benzoylnaphthalene and 14 per cent of the 2-isomer. The ketones were separated by crystallizing from alcohol, the 1-derivative being deposited first.

[337] P. Karrer, E. Epprecht, and Hans König, *Helv. Chim. Acta*, **23**, 272-283 (1940); *C. A.*, **34**, 5435
[338] J. v. Braun, G. Kerschbaum, and H. Schuhman, *Ber.*, **53**, 1155-1173 (1920).
[339] K. Fleischer and F. Seifert, *Ber.*, **53**, 1255-1261 (1920); *Ann.*, **422**, 272-317 (1920).
[340] K. Dziewonski and J. Moszew, *Bull. intern. acad. polonaise sci.*, 1930 A, 66-71; *C. A.*, **25**, 1515 (1931).
[341] British P. 333,666 (1929) to J. Y. Johnson (to I. G. Farbenindustrie); *Brit. Chem. Abstracts*-B, 1017 (1930); *Chem. Zentr.*, 1930, II, 3196.
[342] K. Dziewonski and S. Wodelski, *Rocznik Chem.*, **12**, 366 377 (1932); *Brit. Chem. Abstracts*-A, 839 (1932).
[343] L. Roux, *Ann. chim. (6)*, **12**, 341 (1887).
[344] Rospendowski, *Compt. rend.*, **102**, 572 (1886).
[345] K. Elbs, *J. prakt. Chem. (2)*, **35**, 508 (1887).
[346] P. J. Montagne, *Rec. trav. chim.*, **26**, 273-284 (1907); *J. Chem. Soc. Abs.*, **858** (1907).

Caille [347] prepared the 1-benzoylnaphthalene without the formation of the 2-isomer. Freshly sublimed aluminum chloride was thrown little by little into a carbon disulfide solution of naphthalene and benzoyl chloride, cooled to 0°. It dissolved and the reaction was accompanied by the precipitation of a crystalline addition product. When the reaction was completed, the reaction product was filtered as rapidly as possible and decomposed with iced HCl. The ketone was obtained in 60-80 per cent yield and in such a pure state that a single crystallization was sufficient.

Fieser [348] outlines a method for the preparation of 1-benzoylnaphthalene which is based on that of Perrier.[349] Here an addition compound of benzoyl chloride and aluminum chloride is first obtained by heating together a mixture of equivalent quantities of these substances. Fieser recommends the use of carbon disulfide as solvent. When the solution of the addition compound is somewhat cool, an equivalent quantity of naphthalene is gradually added to it. In order to complete the reaction the mixture is warmed for a few minutes on a steam-bath. Upon cooling in an ice-bath the ketone-aluminum chloride complex solidifies, and it is separated from the reaction mixture by suction filtration. The complex is decomposed with HCl-water and the ketone is extracted with ether. Upon drying and crystallization from ethanol or methanol pure 1-benzoylnaphthalene is obtained.

It is interesting to note that in both the Caille and Perrier preparation of the 1-isomer, carbon disulfide is used as solvent. Fieser points out the fact that regardless of procedure used, a small percentage of the 2-isomer is always formed, but it does not appear in the final product because it is soluble in the carbon disulfide used. The solvent also retains any organic tars which may be formed.

Nenitzescu and co-workers [350] obtained 1-benzoylnaphthalene by heating benzoyl chloride and naphthalene under reflux without the use of a catalyst. According to these investigators, the use of a catalyst makes possible the occurrence of the reaction only at low temperatures; at higher temperatures this and other Friedel-Crafts reactions take place without the use of a catalyst.

The production of a diketone is claimed in a patent to I. G. Farbenindustrie.[351] At 0° naphthalene is first reacted with benzoyl chloride in the presence of aluminum chloride until no more hydrogen chloride is evolved; then a further amount of benzoyl chloride is added, the temperature is raised to 30-40°, and more aluminum chloride is added to the reaction mixture. At the end the mixture is heated to 90-100°. 1,5-Dibenzoylnaphthalene (m.p. 186.5°) is thus obtained in a 70 per cent theoretical yield.

The use of at least twice the equimolecular amount of the benzoyl

[347] E. Caille, *Compt. rend.*, 153, 893-894 (1911); *C. A.*, 5, 3413.
[348] L. Fieser, "Experiments in Organic Chemistry," p. 192, Heath, 1935.
[349] G. Perrier, *Ber.*, 33, 815-818 (1900); *J. Chem. Soc. Abs.*, 78 (I), 331.
[350] C. D. Nenitzescu, D. A. Isacescu and C. N. Ionescu, *Ann.*, 491, 210-220 (1931); *C. A.*, 26, 1257.
[351] French P. 642,907 (1927); British P. 279,506 (1927) to I. G.; *C. Z.*, 1929, I, 2227.

chloride with naphthalene in the presence of aluminum chloride at a temperature of not over 100° also results in the formation of the diacyl derivative. The preparation of 1,5-dibenzoylnaphthalene is thus claimed.[352]

Diacyl derivatives of naphthalene may also be prepared by reacting a monoacyl derivative with an acid chloride. 4-Chloro-1,5-dibenzoylnaphthalene (m.p. 167-168°) is formed by the reaction of 1-benzoylnaphthalene with 4-chlorobenzoyl chloride in carbon disulfide by heating, at 50-55°, with aluminum chloride.[353]

Some reactions of naphthalene with substituted aroyl chlorides are listed in Table 14.

Table 14

Acid Chloride	Product	Ref
4-Chlorobenzoyl	4,4'-dichloro-1,5-dibenzoylnaphthalene	1
3-Chlorobenzoyl	3,3'-dichloro-1,5-dibenzoylnaphthalene	1
3,4-Dichlorobenzoyl	3 4,3',4'-tetrachloro-1,5-dibenzoylnaphthalene	1
2-Methylbenzoyl	1-naphthyl *o*-tolyl ketone	2
3-Methylbenzoyl	1-naphthyl *m*-tolyl ketone	2
4-Chloro-2-methylbenzoyl	4,4'-dichloro-3,3'-dimethyl-1,5-dibenzoyl naphthalene	3
Biphenyl-4-carboxylic	1-naphthyl *p*-xenyl ketone	2
2-Anthraquinonyl carboxylic	2-anthraquinonyl 1-naphthyl ketone 2-anthraquinonyl 2-naphthyl ketone	2
Phenylacetyl	1-naphthyl benzyl ketone 2-naphthyl benzyl ketone	4, 5
Diphenylacetyl	diphenylmethyl naphthyl ketone	6
Terephthalyl	*p*-di-1-naphthoylbenzene	7
Isophthalyl	*m*-di-1-naphthoylbenzene	7

References

1. German P. 576,253 (1933) to I. G.; *C. A.*, 27, 3722
2. R. Scholl and C. Seer, *Ann.*, 394, 111-177 (1912), *C. A.*, 7, 790
3. German P 525,187 (1931) to I G , *C Z* , 1931, II 1933
4. P. Ruggli and M Reinert, *Helv Chim Acta*, 9, 67-79 (1926), *C A* 20, 1401 (1926)
5. J. W. Cook and C L. Hewett, *J Chem Soc* , 365-377 (1934), *C A* , 28, 3413
6. A. McKenzie and W S Denniler, *J Chem Soc* , 125, 2109 (1924)
7. C. Seer and O Dischendorfer, *Monatsh* , 34, 1493-1502 (1913) *J Chem Soc Abs* , 104 (I), 1365 (1913).

1,2,3,4-Tetrahydronaphthalene reacts with benzoyl chloride to give tetrahydronaphthyl phenyl ketone, b.p. 222-233°/12 mm. Care must be taken to use an excess of solvent. Thus to a solution of 20 g each of the hydrocarbon and benzoyl chloride in 50 g of carbon disulfide is added 1000 g of carbon disulfide, and this is then slowly treated with aluminum chloride. The ketone could not be crystallized.[354] With 2-methyl-1-naphthoyl chloride and tetralin there is obtained a 70 per cent yield of 2-methyl-5',6',7',8'-tetrahydro-1,2'-dinaphthyl ketone.[355] The product was crystallized from light petroleum and was found to melt at 122.5-123.5°.

Equal weights of 2-methylnaphthalene and benzoyl chloride with aluminum chloride and carbon disulfide give 2-methyl-1-benzoylnaphtha-

[352] German P. 576,253 (1933) to I. G. Farbenindustrie (to R. Sedlmyr and W. Eckert); *C. A.*, 27, 3722 (1933); *C. Z.*, 1933, II, 619.
[353] German P. 525,187 (1931) to I G Farbenindustrie; *C Z* , 1931, II, 1933.
[354] W. Scharwin *Ber.*, 35, 2511-2515 (1902)
[355] J. W. Cook, *J. Chem. Soc,*, 499-507 (1931).

lene.[356] Likewise from 1-naphthoyl chloride and 1-methylnaphthalene in carbon disulfide under the action of aluminum chloride is obtained 4-methyl-1,1′-dinaphthyl ketone.[357]

Clar[358] reports that the action of 1-naphthoyl chloride on 2-methyl naphthalene in the presence of aluminum chloride and carbon disulfide affords 2-methyl-1,1′-dinaphthyl ketone (m.p. 140-141°) in about 90 per cent yield, and that 2-naphthoyl chloride and 2-methylnaphthalene gave 2-methyl-1,2′-dinaphthyl ketone, m.p. 170-171°. The preparation was repeated by Fieser and Dietz,[359] who found that 2-methyl-1,1′-dinaphthyl ketone melted at 171°, and 2-methyl-1,2′-dinaphthyl ketone at 142-143°.

2-Benzoylbenzoyl chloride and 1- or 2-methylnaphthalene give phthalides with aluminum chloride in carbon disulfide. Phenyl-2-methylnaphthylphthalide and phenyl-4-methyl-1-naphthylphthalide, respectively, are obtained.[360]

Due to the directive influence of two methyl groups, 2,6-dimethylnaphthalene easily condenses with an excess of benzoyl chloride to give a diketone. Thus Clar and co-workers[361] added, under cooling, 220 g of aluminum chloride to a solution of 52 g of 2,6-dimethylnaphthalene and 170 g of benzoyl chloride in 700 g of carbon disulfide to obtain 1,5-dibenzoyl-2,6-dimethylnaphthalene, m.p. 262.5-264°. No homogeneous product could be obtained when 2,7-dimethylnaphthalene was substituted for the 2,6-isomer. However, the condensation at 2,7-dimethylnaphthalene with 1-naphthoyl chloride has been found to give 2,7-dimethyl-1,1′-dinaphthyl ketone in 70 per cent yield. The general procedure used here was to treat slowly, under cooling, a suspension of 1 part of the hydrocarbon and 1 part of the acid chloride in 3 parts of carbon disulfide with 1 part of aluminum chloride. The reaction mixture was agitated during addition of the catalyst, and occasionally stirred while subsequently kept in ice for three to six hours.[362] Using this same procedure, the following compounds were also prepared:

2,6-dimethyl-1,1′-dinaphthyl ketone, 50 per cent yield from 2,6-dimethylnaphthalene and 1-naphthoyl chloride.
4-benzoyl-1,6-dimethylnaphthalene, 21 g from 15.6 g of 1,6-dimethylnaphthalene and 14 g of benzoyl chloride.
2,4′-dimethyl-1,1′-dinaphthyl ketone, poor yield from 2-methylnaphthalene and 4-methyl-1-naphthoyl chloride.
2,7,4′-trimethyl-1,1′-dinaphthyl ketone, 45 per cent yield from 2,7-dimethylnaphthalene and 4-methyl-1-naphthoyl chloride.

Scholl and co-workers[363] obtained 2,6-dimethyl-1-benzoylnaphthalene in 32 per cent yield from dimethylnaphthalene, benzoyl chloride, and aluminum chloride.

[356] F. Mayer and A. Sieglitz, *Ber.*, **55**, 1835-1859 (1922); L. F. Fieser and E. M. Dietz, *Ber.*, **62**, 1827-1833 (1929).
[357] J. W. Cook and A. M. Robinson, *J. Chem. Soc.*, 505-513 (1938).
[358] E. Clar, *Ber.*, **62**, 350-359 (1929); *Brit. Chem. Abstracts-A*, 435 (1929).
[359] L. F. Fieser and E. M. Dietz, *Ber.*, **62**, 1827-1833 (1929).
[360] E. Clar, *Ber.*, **63**, 112-120 (1930); *Brit. Chem. Abstracts-A*, 334 (1930).
[361] E. Clar, H. Wallenstein, and R. Avenarius, *Ber.*, **62**, 950-955; *C. A.*, **23**, 3915 (1929).
[362] J. W. Cook, *J. Chem. Soc.*, 489-499 (1931).
[363] R. Scholl, *Ber.*, **68**, 2034-2039 (1935).

When 1-methylnaphthalene was reacted in the cold with phenylacetyl chloride in the presence of aluminum chloride in carbon disulfide, Cook and Galley [364] obtained 1-phenylacetyl-4-methylnaphthalene, m.p. 59-61°.

Terephthalyl and isophthalyl chlorides give normal Friedel-Crafts disubstitution products with 1- or 2-methylnaphthalene when 2 moles of hydrocarbon are used, but one mole of 2-methylnaphthalene gives *p*-2-methyl-1-naphthoylbenzoic acid when reacted with terephthalyl chloride.[365]

An I. G. Farbenindustrie patent [366] claims the reaction of 1-benzylnaphthalene with benzoyl chloride to yield 4-benzoyl-1-benzylnaphthalene, m.p. 110°. Benzene was used as the solvent, and temperatures of 5-30° were used. Treatment of 1-(4'-chlorobenzyl)naphthalene with benzoyl chloride likewise gives the corresponding 4-benzoyl compound, m.p. 118°.

The reaction of aromatic acid halides with di- and polyhalogenated naphthalenes has been claimed.[367] Thus, a mixture of 20 parts of 1,4-dichloronaphthalene, 16 parts of benzoyl chloride, 35 parts of aluminum chloride and 130 parts of carbon disulfide was boiled with stirring for seven hours. After usual treatment of the reaction mixture there was obtained 1,4-dichloro-8-benzoylnaphthalene, m.p. 104-105°. The same product is also formed if benzoyl chloride is used as diluting agent. In this case the reaction mixture is heated for eight hours at 160°. In the same way the preparation of the following is claimed:

1,5-dichloro-8-benzoylnaphthalene, m.p. 112°
1,4-dichloro-8-(*p*-chlorobenzoyl)naphthalene, m.p. 118°
1,4-dichloro-8-(*o*-chlorobenzoyl)naphthalene, m.p. 122-123°
1,4-dichloro-8-(α-naphthoyl)naphthalene, m.p. 163-164°
1,4-dichloro-8-(β-naphthoyl)naphthalene
1,4-dichloro-8-(*p*-tolyl)naphthalene, m.p. about 135°
1,4-dichloro-8-(*o*-tolyl)naphthalene, m.p 91-92°

Biphenyl and Aryl Methanes

Phosgene and biphenyl react in the presence of aluminum chloride with replacement of both chlorines to give 4,4'-diphenylbenzophenone (m.p. 229°) according to the scheme [368]:

$$COCl_2 + 2C_6H_5.C_6H_5 \longrightarrow (C_6H_5.C_6H_4)_2CO + 2HCl$$

Acetyl chloride and biphenyl readily undergo Friedel-Crafts reaction to yield 4-acetyl biphenyl.[369]

Diacetylation may be secured. Recently, Silver and Lowy [370] made a

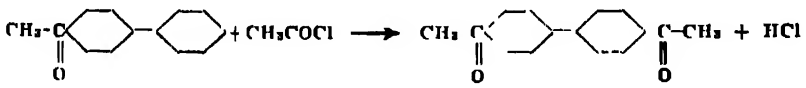
[364] J. W. Cook and R. A. E. Galley, *J. Chem. Soc.*, 2012-2018 (1931); *Brit. Chem. Abstracts* A, 1157 (1931).
[365] E. Clar, F. John, and R. Avenarius, *Ber.*, 72, 2179-2147 (1939).
[366] British P. 339,666 (1929) to J. Y. Johnson (to I. G. Farbenindustrie); *Brit. Chem. Abstracts*-B, 1017 (1930); *Chem. Zentr.*, 1930, II, 3196.
[367] German P. 495,332 (1927) to I. G.; *C. A.*, 24, 3248; French P. 664,010 (1929) to I. G.; *C. A.* 1930, *I*, 1221; British P. 301,311 (1928) to I. G.; *Brit. Chem. Abstracts*-B, 349 (1930).
[368] P. Adam, *Ann. chim. phys. (6)*, 15, 258 (1888).
[369] P. Adam, *Compt. rend.*, 104, 991-993 (1887); *J. Chem. Soc. Abs.*, 52, 689 (1887); *Ann. chim. phys. (6)*, 15, 258 (1888).
[370] S. L. Silver and A. Lowy, *J. Am. Chem. Soc.*, 56, 2429-2431 (1934); *C. A.*, 29, 767.

study of Friedel-Crafts type reactions on biphenyl, and reported that the product of the reaction of biphenyl with acetyl chloride was *p,p'*-diacetylbiphenyl (m.p. 191°) which they secured in a 43 per cent yield. The diacetylation here was due to the fact that large excesses of the acetyl chloride and of aluminum chloride were used; the weight of acetyl chloride was 2½ times that of the biphenyl and a six-fold quantity of aluminum chloride was employed.

Chloroacetyl chloride was reacted with biphenyl by Collet.[371] 4-Chloroacetylbiphenyl (m.p. 122-123°) was produced by dissolving 10 g of biphenyl in carbon disulfide and reacting this with 10 g of anhydrous aluminum chloride and 8 g of chloroacetyl chloride. The reaction proceeded as follows:

$$C_6H_5C_6H_5 + ClCH_2COCl \xrightarrow{AlCl_3} C_6H_5C_6H_4COCH_2Cl + HCl$$

An excess of chloroacetyl chloride was reacted with biphenyl in the presence of an excess of anhydrous aluminum chloride by Silver and Lowy.[372] They obtained a diketone, *p,p'*-bis-(chloroacetyl)biphenyl (m.p. 228-229°) in 35 per cent yield. In this reaction, as well as that of biphenyl with acetyl chloride, the aluminum chloride was suspended in a solution of one of the reagents in a suitable volume of carbon disulfide, and the other reagent was added slowly to this from a dropping funnel. The mixture was refluxed on a water-bath until completion of the reaction. In the same way, they reacted methyl *p*-xenyl ketone and acetyl chloride in theoretical proportions, and obtained *p-p'*-diacetylbiphenyl:



An analogous reaction occurred with chloromethyl *p*-xenyl ketone and chloroacetyl chloride.

Willgerodt and Scholtz[373] reacted equal molecular quantities of biphenyl and propionyl chloride in the presence of aluminum chloride and carbon disulfide and obtained *m*-propionylbiphenyl, $C_6H_5C_6H_4COC_2H_5$, m.p. 89°, b.p. 344°. It is noteworthy that in the case of the other acylations reported, substitution occurred in the *p*-position.

Following the procedure used by these workers, Machlis and Blanchard[374] secured what they showed to be the expected *p*-compound; they obtained a practically theoretical yield of not *m*-, but *p*-propionylbiphenyl from biphenyl and propionyl chloride. *p*-Propionylbiphenyl melts at 97°; upon oxidation it is converted to *p*-phenylbenzoic acid.

Biphenyl or substituted biphenyls have been reacted with stearoyl

[371] A. Collet, *Bull. soc. chim. (3)*, 17, 306-310 (1897); *J. Chem. Soc. Abs.*, 76, 55-56 (1899).
[372] S. I. Silver and A. Lowy, *J. Am. Chem. Soc.*, 56, 2429-2431 (1934); *C. A.*, 29, 707.
[373] C. Willgerodt and T. Scholtz, *J. prakt. Chem. (2)*, 81, 382-402 (1910); *J. Chem. Soc.* 1910 (I), 302.
[374] S. Machlis and K. C. Blanchard, *J. Am. Chem. Soc.*, 57, 176-177 (1935).

chloride and other higher fatty acid chlorides to give xenyl alkyl ketones.[375] The following have been secured:

xenyl heptadecyl ketone, m.p. 108-109°
xenyl tridecyl ketone, m.p. 102-103°
xenyl undecyl ketone, m.p. 97-98°
p-methylxenyl heptadecyl ketone, m.p. 105-106°
chloroxenyl heptadecyl ketone, m.p. 96-97°

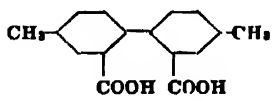
Other ketones which have been prepared by reaction with higher fatty acid halides include the following *p*-xenyl ketones [376]:

	m.p.
lauric	101-102°
myristic	102-103°
palmitic	103-104°
stearic	106-107°

Heptadecyl xenyl ketone, prepared from stearoyl chloride and biphenyl at 0°, and carefully purified, has been shown to melt at 106-107°.[377]

Oxalyl chloride with biphenyl in the presence of aluminum chloride and carbon disulfide gives a 75 per cent theoretical yield of *p*-biphenyl carboxylic acid, carboxylation occurring because of the instability of oxalyl chloride in the presence of aluminum chloride.[378]

Whereas biphenyl and oxalyl chloride easily yield the monocarboxylic acid, similar reaction with *p,p'*-bitolyl (*p,p'*-dimethylbiphenyl) gives mainly the dicarboxylic acid, together with a small amount of the monocarboxylic acid and a large amount of *p,p'*-dimethylphenanthrenequinone; whereas biphenyl gives no quinone. The reaction with *o,o'*-bitolyl and with *m,m'*-bitolyl gave the corresponding dicarboxylic acids, together with some monocarboxylic acid, but no quinones were formed. The behavior of 4,4',2,2'-bixylyl was similarly investigated. Here two methyl groups are *para*, and two are *ortho*, but no quinone was obtained. The formation of the quinone from *p,p'*-bitolyl may be due to the fact that the directing influence of the methyl groups present causes formation of *p,p'*-dimethyl-biphenyl-*o,o'*-dicarboxylic acid,

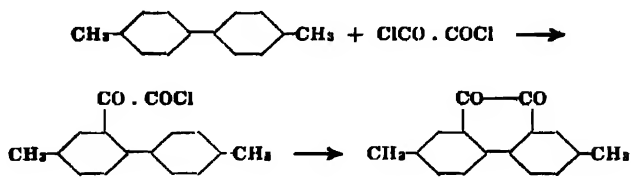


With the other substituted biphenyls, steric hindrance prevented the introduction of the carboxyl groups in the 2,2'-position.

The formation of the quinone may be caused by the fact that, due to the activating influence of the two methyl groups, some reaction occurred with oxalyl chloride before its decomposition into phosgene and carbon

[375] U. S. P. 2,033,541 (1936) to A. W. Ralston and C. W. Christensen (to Armour and Company) *C. A.*, 30, 3134.
[376] G. M. Ford, *Iowa State Coll. J. Sci.*, 12, 121-122 (1937); *C. A.*, 32, 4943.
[377] L. A. Mikeska, C. F. Smith and E. Lieber, *J. Org. Chem.*, 2, 499-505 (1938).
[378] C. Liebermann and M. Zsuffa, *Ber.*, 44, 852-865 (1911).

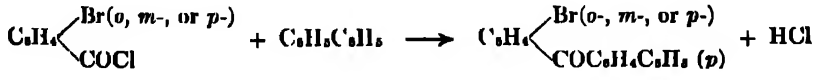
monoxide by the catalyst present. Condensation with oxalyl chloride first occurred, followed by ring closure [379]:



Biphenyl with fumaryl chloride and aluminum chloride in benzene solution gives bis(*p*-phenylbenzoyl)ethylene, m.p. 247.5-248°. The reaction occurred by keeping the mixture at room temperature for one day.[380] In 1881, Wolf [381] reacted biphenyl with benzoyl chloride in the presence of aluminum chloride and obtained a resinous body containing a dibenzoylbiphenyl, $C_{12}H_8(C_6H_5CO)_2$, and possibly two monobenzoyl biphenyls, $C_{12}H_9(C_6H_5CO)$.

The preparation of 4-benzoylbiphenyl from biphenyl, benzoyl chloride, and aluminum chloride in carbon disulfide has been reported by various workers.[382]

Equimolecular amounts of halogen-substituted benzoyl chloride and biphenyl give the correspondingly halogenated phenylbenzophenones. Thus Gomberg and Bailar [383] prepared 4-bromo-4′-phenylbenzophenone, 3-bromo-4′-phenylbenzophenone, and 2-bromo-4′-phenylbenzophenone according to the reaction:



Here the acid chloride from 20 g of the corresponding bromobenzoic acid was dissolved in 150 cc of carbon disulfide, 20 g of biphenyl was added, and then 16 g of aluminum chloride, in small portions. The mixture was warmed on a steam-bath for three days and subjected to usual treatment. The yields were *o*- bromo-, 65 per cent; *m*-, 75 per cent; *p*-, 55 per cent.

With *p*-toluyl chloride, in the presence of aluminum chloride in carbon disulfide, *p*-tolyl xenyl ketone (m.p. 133-134°) is formed.[384] Phenylacetyl chloride and biphenyl react to give benzyl xenyl ketone, $C_6H_5CH_2$-$COC_6H_4C_6H_5$, m.p. 149°.[385]

Cinnamoyl chloride, in spite of its double bond, reacts as do other monocarboxylyl chlorides with biphenyl. Bachmann and Wiselogle [386]

[379] C. Liebermann, *Ber.*, 44, 1453-1455 (1911).
[380] H. G. Oddy, *J. Am. Chem. Soc.*, 45, 2156-2160 (1923).
[381] N. Wolf, *Ber.*, 14, 2031-2032 (1881).
[382] D. Hey and E. R. R. Jackson, *J. Chem. Soc.*, 802-806 (1936); H. Staudinger and N. Kon, *Ann.*, 384, 97 (1911); *C. Z.*, 1911, II, 1686. J. F. Norris, R. Thomas, and B. M. Brown, *Ber.*, 43, 2956 (1910).
[383] M. Gomberg and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 51, 2233 (1929).
[384] W. Schlenk and E. Bergmann, *Ann.*, 463, 22-34 (1928); *C. A.*, 22, 4500.
[385] M. Delaville, *Compt. rend.*, 184, 463 (1927).
[386] W. E. Bachmann and F. Y. Wiselogle, *J. Am. Chem. Soc.*, 56, 1359-1360 (1934).

obtained 4'-phenylchalcone (m.p. 156°) apparently according to the following equation:

$$C_6H_5CH{:}\,CHCOCl + C_6H_5C_6H_5 \qquad C_6H_5CH{:}\,CHCOC_6H_4C_6H_5 + HCl$$

With naphthoyl chloride, biphenyl yields *p*-xenyl 1-naphthyl ketone, m.p. 142°. Here, too, aluminum chloride in carbon disulfide is used.[387] Scholl and Seer [388] secured a 48 per cent yield in this reaction.

The condensation of biphenyl with 2-methyl-1-naphthoyl chloride with carbon disulfide and aluminum chloride by boiling for three hours leads to the formation of 1-(4'-phenylbenzoyl)2-methylnaphthalene, together with some corresponding diketone.[389]

Biphenyl and an aromatic dicarboxylic acid chloride may react, with substitution of both chlorine atoms. Thus Schlenk and Brauns [390] report the preparation of 1,4-bis(4-phenylbenzoyl)benzene from terephthalic chloride and biphenyl. Pawlewski [391] reacted phthalic acid dichloride with biphenyl and obtained dixenylphthalide. Here the acid chloride reacted as a lactone.

p-Xenylsulfonyl chloride, biphenyl, and aluminum chloride in carbon tetrachloride yield di-*p*-xenyl sulfone.[392]

1,1'-Binaphthyl undergoes normal condensation with benzoyl chloride and aluminum chloride in carbon disulfide, giving 4,4'-dibenzoyl-1,1'-binaphthyl.[393]

Duval [394] worked on the reaction of diphenylmethane in carbon disulfide solution with acetyl chloride in the presence of anhydrous aluminum chloride and reported the production of a mixture of acetophenone, 4-acetyldiphenylmethane, $CH_3COC_6H_4.CH_2C_6H_5$ (m.p. 39°) and 4,4'-diacetyldiphenyl methane, m.p. 93°. The acetophenone could have been formed only by the displacement of the benzyl group through the acetyl group under the influence of the aluminum chloride. Later [395] he checked the constitution of the compounds formed and determined the formation of still another compound, benzyl-4,4'-diacetyldiphenylmethane, m.p. 125°.

Diphenylmethane is carboxylated by reaction with oxalyl chloride and aluminum chloride in carbon disulfide solution.[396] The products, the total yield of which is 80-90 per cent of theoretical, are diphenylmethane-4-monocarboxylic acid and diphenylmethane-4,4'-dicarboxylic acid. Triphenylmethane reacts similarly, mono-, di-, and tricarboxylic acids being

[387] J. Schmidlin and A. Garcia-Banus *Ber.*, 45, 3183-3188 (1912); *J. Chem. Soc Abs.*, 104 (I) 3[illegible] (1913).
[388] R. Scholl and C. Seer, *Ann.*, 394, 149 (1912).
[389] J. W. Cook, *J. Chem. Soc.*, 499-507 (1931).
[390] W. Schlenk and M. Brauns, *Ber.*, 46, 4061-4066 (1913).
[391] Br. Pawlewski, *Ber.*, 28, 513-514 (1895)
[392] H. Kucsynski, L. Kucsynski, and E. Sucharda, *Roczniki Chem.*, 18, 525-50 (1938), *C* 1, 34, 3346.
[393] R. Scholl and C. Seer, *Ann.*, 394, 111-177 (1912); *C. A.*, 7, 790; *Ann.*, 398, 82-96 (1913), *C* 1 7, 2549.
[394] H. Duval, *Compt. rend.*, 146, 341-343 (1908); *J. Chem. Soc. Abs.*, 1908 (I), 277; *C* 1 2, 1668 (1908).
[395] H. Duval, *Bull soc. chim.*, 7, 796-800 (1910); *C. A.*, 2, 1698, 2687; *C. A.*, 4, 2947 (1910), *C* 1 1910, II, 1223.
[396] C. Liebermann and co-workers, *Ber.*, 45, 1186-1217 (1912).

formed. Triphenylmethane monocarboxylic acid was formed in such small amounts, however, that it could not be isolated. A like reaction occurs with bibenzyl, the products being bibenzyl-4-monocarboxylic acid (m.p. 173-174°) and bibenzyl-4,4'-dicarboxylic acid, m.p. over 320°.

Reaction of triphenylmethane with benzoyl chloride and aluminum chloride in carbon disulfide results in mono-acylation, the product being 4-benzoyltriphenylmethane.[397]

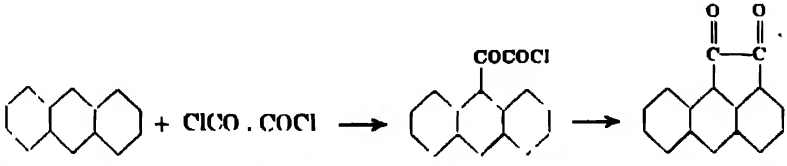
Anthracene

The condensation of anthracene with aliphatic acid chlorides is claimed by various patents to I. G. Farbenindustrie. A mixture of 1- and 2-anthracyl methyl ketone is claimed as the product when to a mixture consisting of 1000 parts by weight of benzene, 178 of anthracene, and 234 of acetyl chloride was added, under stirring and cooling, to 0-10°, 400 parts of aluminum chloride. The mixture was then stirred without cooling for four to five hours.[398] After distillation, the 1- and 2-isomer may be separated by fractional crystallization. The 1-isomer melts at 103-105°, and the 2-isomer at 183-185°.

Using nitrobenzene as the solvent, and temperatures of 10-15°, a mixture of 1- and 2-propionylanthracene was similarly prepared from propionyl chloride and anthracene. The 1-compound melts at 150° and the 2-compound at 162-163°.[399] The preparation of two diacetylanthracenes, one melting at 212-215° and the other at 173°, is claimed in the same patent.

Under milder conditions than those described above in the preparation of the 1- and 2-anthracyl alkyl ketones, the condensation of acetyl- and propionylchloride with anthracene results in the formation of 9-anthracyl methyl ketone (m.p. about 80°) and 9-anthracyl ethyl ketone (m.p. about 78°) respectively.[400]

The reaction of anthracene with oxalyl chloride and aluminum chloride has been much studied.[401] During the reaction oxalyl chloride is decomposed into phosgene and carbon monoxide, so that carboxylation of the anthracene takes place; however, reaction with oxalyl chloride also occurs, with introduction of the CO.COCl radical; simultaneous ring closure results in formation of a quinone:

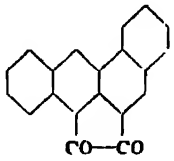


[397] A. E. Tschitschibabin, *Ber.*, 40, 3969 (1907); 41, 2423; *J. Russ. Phys.-Chem. Soc.*, 39, 1160; 40, 1369.
[398] French P. 683,071 (1930) to I. G. Farbenindustrie; *C. Z.*, 1930, I, 2209.
[399] German P. 493,247 (1926) to Arthur Lüttringhaus and Filip Kačer (to I. G. Farbenindustrie); *C. A.*, 24, 2472; *C. Z.*, 1930, I, 2881.
[400] British P. 289,385 (1927) to I. G. Farbenindustrie; U. S. P. 1,766,448 to I. G. Farbenindustrie; *C. A.*, 23, 715. German P. 493,868 (1926) to Arthur Lüttringhaus and Filip Kačer (to I. G. Farbenindustrie); *C. A.*, 24, 2757; *C. Z.*, 1930, I, 3486.
[401] C. Liebermann and M. Zsuffa, *Ber.*, 44, 201-210 (1911); C. Liebermann and co-workers, *Ber.*, 45, 1196-1217 (1912).

That formation of the quinone predominates is evident from the fact that from 10 g of anthracene there is obtained 9 g of aceanthraquinone and 3 g of anthroic acid.

Oxalyl chloride reacts similarly with bianthryl, the chief product being a diquinone, together with a small amount of acid.[402]

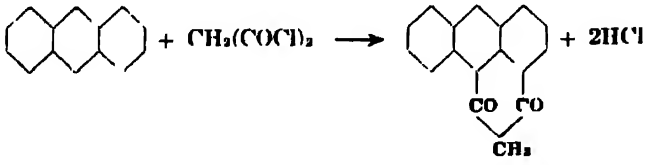
The formation of an acid and a quinone also occurs upon treatment of β-methylanthracene with oxalyl chloride and aluminum chloride. Here the chief product is a methylaceanthraquinone, and the secondary product is a β-methylanthracene carboxylic acid.[403] With 1,2-benzanthracene the products are also an acid and a quinone.[404] 1,2-Benzanthracene carboxylic acid and 1,2-benzaceanthrene quinone are formed. The quinone probably has the structure:



The reaction of α- or β-chloroanthracene also yields acids and quinones, chloroanthracene carboxylic acids and chloroaceanthrenequinones being formed.[405] Dichloroanthracenes react similarly.

Phosgene has been reported to react with anthracene at 180-200° to yield some anthracene-9-carboxylic acid chloride.[406] At 240-250° 10-chloroanthracene-9-carboxylic acid chloride is formed.[407]

The condensation of malonyl chloride with anthracene is reported by Kardos,[408] the reaction proceeding:

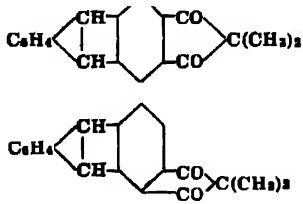


The anthracene-1,9-indandione which was obtained darkens at 250° and melts, under decomposition, at 280°. This preparation, as well as that of malonylmethylanthracene (from 2-methylanthracene and malonyl chloride) is claimed in a patent which was subsequently issued to him.[409]

Dimethylmalonyl chloride and anthracene[410] yield anthracenedi-

[402] C. Liebermann, M. Kardos, and G. Muhle, *Ber.*, **48**, 1648-1653 (1915); *J. Chem. Soc.* **110** (I), 50 (1916).
[403] A. Dansi and A. Semproni, *Gazz. chim. ital.*, **66**, 182-186 (1936); *C. A.*, **31**, 1022, also C. Liebermann and co-workers, *Ber.*, **45**, 1186-1217 (1912).
[404] A. Dansi, *Gazz. chim. ital.*, **67**, 85-88 (1937); *C. A.*, **31**, 6227.
[405] C. Liebermann and co-workers, *Ber.*, **45**, 1186-1217 (1912).
[406] C. Gräbe and C. Liebermann, *Ber.*, **2**, 678-679 (1869).
[407] G. Bohla, *Ber.*, **20**, 701-708 (1887).
[408] M. Kardos, *Ber.*, **46**, 2090 (1913).
[409] German P. 275,248 to M. Kardos, *C. Z.*, 1914, II, 278.
[410] Martin Freund and K. Fleischer, *Ann.*, **399**, 182-241 (1913); *C. A.*, **7**, 3737.

methylindandione (m.p. 148.5-149°) having one of the two following structures:



With diethylmalonyl chloride, one diethylanthraceneindandione (m.p. 104-105°) was obtained.[411]

The reaction of anthracene with benzoyl chloride in the presence of aluminum chloride and carbon disulfide are studied by Lippmann and Fleissner.[412] They reported that about 50 per cent of the anthracene was converted into anthraphenone which melted at 135-140°, obviously an impure product. Perrier [413] pointed out that previously,[414] in this reaction he had secured an anthraphenone which melted at 143° as well as two other compounds, m.p. 75° and 203°. Accordingly, Lippmann and Keppich [415] modified their method of procedure and repeated the reaction, using this time aluminum chloride containing about 10 per cent of the hydrated salt. They determined the melting point of pure *meso*-anthraphenone to be 148°, securing 28 per cent of theoretical yield.[416] A large portion of the anthracene was converted into the impure ketone which could not easily be purified.

In preparing *meso*-anthraphenone, Krollpfeiffer [417] preferred to use nitrobenzene as the solvent. Twenty g of anthracene was dissolved in 200 g of the solvent; to this, under cooling, 30 g of aluminum chloride was added. After cooling to about −10°, 8 g of benzoyl chloride was added. About 25 g of the anthraquinone was obtained.

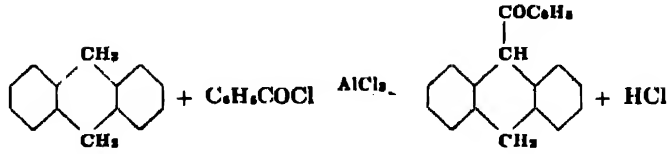
Cook [418] claims that better yields of the pure *meso*-anthraphenone are obtained by using benzoic anhydride instead of benzoyl chloride in the Friedel-Crafts condensation.

Nenitzescu and co-workers [419] obtained almost quantitative yields of 9-benzoylanthracene (*meso*-anthraphenone) by heating benzoyl chloride with anthracene in nitrobenzene without the use of a catalyst.

In an attempt to prepare 2-benzoylanthracene, in order to characterize the products obtained by Perrier,[414] Nenitzescu and co-workers [420] reacted dihydroanthracene with benzoyl chloride, hoping to get 2-benzoyltetrahydroanthracene which they could subsequently dehydrogenate to 2-benzoylanthracene. The acylation proceded in a very unexpected man-

[411] M. Freund and K. Fleischer, *Ann.*, 373, 291-336 (1910); *J. Chem. Soc. Abs.*, 98 (I), 490 (1910).
[412] E. Lippmann and F. Fleissner, *Ber.*, 32, 2249 (1899).
[413] G. Perrier, *Ber.*, 33, 816 (1900).
[414] G. Perrier, Thèse inaugurale de la Faculté des Sciences de Paris, 1896.
[415] E. Lippmann and P. Keppich, *Ber.*, 33, 3086-3092 (1900).
[416] E. Lippmann and I. Pollak, *Ber.*, 34, 2766 (1901).
[417] F. Krollpfeiffer, *Ber.*, 56, 2360-2365 (1923).
[418] W. Cook, *J. Chem. Soc.*, 1282-1287 (1926).
[419] C. D. Nenitzescu, D. A. Isacescu, and D. N. Ioncscu, *Ann.*, 491, 210-220 (1931); *C. A.*, 26, 1257.
[420] C. D. Nenitzescu, Ion Gavat, and Dumitru Cocora, *Ber.*, 72, 819-820 (1939).

ner, however, the acyl group replacing the labile hydrogen in the CH_2 group:



The 9-benzoyl-9,10-dihydroanthracene (m.p. 104°) was obtained in good yield. Acylation with acetyl chloride analogously gave 9-acetyl-9,10-dihydroanthracene, a thick oil, b.p. 150-151°/3 mm. The course of the reaction is very unusual in that ordinarily the CH_2 group in dihydroanthracene shows no especial reactivity.

The condensation of anthraquinone carboxylyl chlorides with anthracene has been studied by de Diesbach, Lempen, and Benz.[421]

Higher Polynuclear Hydrocarbons

Within recent years, acylation of polynuclear hydrocarbons has become of great interest in connection with investigation of carcinogenic hydrocarbons.

Willgerodt and Albert[422] reacted phenanthrene in carbon disulfide with acetyl chloride in the presence of aluminum chloride. They obtained 9-acetylphenanthrene, m.p. 123°. Using an excess of acetyl chloride they obtained the diketone, 9,10-diacetylphenanthrene, m.p. 178°. Later, when Mosettig and de Kamp[423] tried to prepare 9-acetylphenanthrene in the same way they were not able to obtain the ketone. With much difficulty, however, they did isolate very small amounts of two ketones, m.p. 72 and 143°. With a view to securing a better method of preparation, they lowered the temperature to 0° or to −15°, but obtained no better results. Substitution of other catalysts, or of acetyl bromide or acetic anhydride for the acetyl chloride likewise did not improve the yield. Using nitrobenzene instead of carbon disulfide as solvent, however, they obtained a mixture of two ketones in about an 80 per cent yield. These were separated by difference of solubility in methyl and ethyl alcohol. 2-Acetylphenanthrene, sparingly soluble in alcohol, melts at 143°, and was secured in 15 per cent yield. 3-Acetylphenanthrene (m.p. 72°) was obtained in 63.5 per cent yield. They were not able to isolate any other acetylphenanthrene isomer. Attempts to synthesize 9-acetylphenanthrene by other means were fruitless; there was a marked favoring of the 2- and 3-positions in the Friedel-Crafts acetylation.

Similarly in the reaction of propionyl chloride with phenanthrene

[421] H. deDiesbach, H. Lempen, and H. Benz, *Helv. Chim. Acta.*, 15, 2141-2150 (1932). *C. A.* 27, 257
[422] C. Willgerodt and B. Albert, *J. prakt. Chem.*, 84 (II), 283-294 (1911). *J. Chem. Soc.* 100, 1911, I, 882; *C. A.*, 6, 80
[423] E. Mosettig and J. van de Kamp, *J. Am. Chem. Soc.*, 52, 3704-3710 (1930). For the acylation of 4-methylphenanthrene, see W. E. Bachmann and R. O. Edgerton, *J. Am. Chem. Soc.*, 62, 2210-2 (1940).

Bachmann and Struve [424] obtained 2- and 3-propionylphenanthrene. To an ice-cold solution of 320 g of aluminum chloride and 200 g of phenanthrene in 1750 cc of nitrobenzene was added 140 g of propionyl-chloride at one time. The mixture was kept cold for half an hour and allowed to stand at room temperature for twelve hours. After usual treatment with water-HCl and removal of solvent, the product was dissolved in a hot mixture of acetone and alcohol. From this, 20 g of 2-propionylphenanthrene crystallized out. Recrystallization from alcohol gave a m.p. of 104-105°. From the filtrate from which the 2-isomer had been removed, 60 g of 3-propionylphenanthrene was deposited after three weeks' standing. Recrystallization from alcohol gave a m.p. of 55-57°.

The condensation of phenanthrene with diethylmalonyl chloride in the presence of aluminum chloride yields diethylphenanthreneindandione, $C_{21}H_{18}O_2$, m.p. 137-139°.[425]

The reaction between phenanthrene and benzoyl chloride has been studied by Bachmann.[426] It had been previously reported by Willgerodt and Albert [422] that the reaction of phenanthrene and benzoyl chloride in carbon disulfide solution in the presence of aluminum chloride gives 9-benzoylphenanthrene, m.p. 127°. Bachmann repeated the reaction, exactly as described by the previous workers, and obtained 1-benzoylphenanthrene, m.p. 146-148°. When the reaction was performed in nitrobenzene solution there was obtained, besides the 1-isomer, small amounts of 2- and 3-benzoylphenanthrene. The 2-isomer recrystallized from acetone melts at 111-112°. Using the Perrier modification of the Friedel-Crafts reaction, 25 g of 1 benzoylphenanthrene was obtained from 114 cc of benzoyl chloride and 204 g of phenanthrene. In nitrobenzene solution, the reaction yielded from 100 g of phenanthrene, 32 g of 3-benzoylphenanthrene, 5 g of the 2-, and 10 g of the 1-isomer. The compound reported by Willgerodt and Albert was not found.

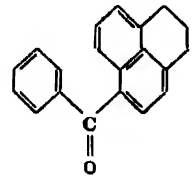
A dibenzoyl derivative (m.p. 181°) has also been obtained by the reaction of phenanthrene with benzoyl chloride and aluminum chloride in carbon disulfide.[427]

Clar [428] reacted phenanthrene with *o*-toluyl chloride in carbon disulfide solution in the presence of aluminum chloride. He was able to get no crystalline product, but concluded that the product consisted mostly of 9-*o*-toluylphenanthrene, together with small amounts of the 2- and 3-isomers. By performing the reaction in nitrobenzene solution, however, Bachmann and Pence [429] found that a mixture of 2-*o*-toluylphenanthrene and 3-*o*-toluylphenanthrene was obtained which could be readily separated into its crystalline components, m.p. 115-116° and 89-90°, respectively.

Perinaphthane (*peri*-trimethylenenaphthalene) has been reacted with benzoyl chloride by the Perrier modification of the Friedel-Crafts reac-

[424] W. E. Bachmann and W. S. Struve, *J. Am. Chem. Soc.*, 56, 1658-1661 (1934); *C. A.*, 30, 7569.
[425] M. Freund and K. Fleischer, *Ann.*, 373, 291-336 (1910); *J. Chem. Soc. Abs.*, 98 (I), 490 (1910).
[426] W. E. Bachmann, *J. Am. Chem. Soc.*, 57, 555-559 (1935).
[427] W. Dilthey, S. Henkels, and M. Leonard, *J. prakt. Chem.*, 151, 97-126 (1938); *C. A.*, 32, 3396.
[428] E. Clar, *Ber.*, 62, 350-359 (1929); *Ber.*, 62, 1574-1582 (1929).
[429] W. E. Bachmann and L. H. Pence, *J. Am. Chem. Soc.*, 57, 1130-1131 (1935).

tion.[430] A 95 per cent yield of 3-benzoylperinaphthane (m.p. 62-63°) having the following structure was obtained:



The synthesis of an acetylretene (m.p. 99.5-100°) has been reported in 60 per cent yield by reaction of retene, acetyl chloride, and aluminum chloride in carbon disulfide solution.[431] A 45 per cent yield has been obtained using nitrobenzene as solvent, and it has been shown to be 3-acetylretene.[432]

The reaction of retene with acetyl chloride and aluminum chloride in nitrobenzene solution for the production of acetylretene has been patented.[433]

Present availability of retene from rosin and pine tar oils suggests its employment for synthesis in the phenanthrene series.

The acetylation of 9,10-dihydroretene has also been studied, and it has been found to occur readily. The product is β-acetyldihydroretene (m.p. 77°) secured in 60 per cent yield, but if slightly more than twice the quantity of acetyl chloride and of the catalyst is used, a 60 per cent yield of the diacetyl derivative (m.p. 147-148°) was obtained. The structure of this product has not been proved.[434] Oxalyl chloride introduces the carboxyl group into retene, the reaction product of retene, oxalyl chloride and aluminum chloride in carbon disulfide being retene monocarboxylic acid.[435]

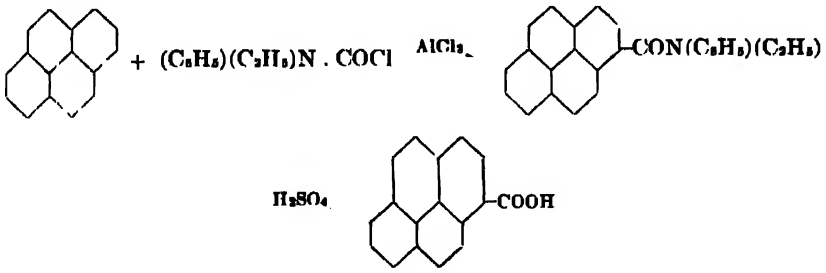
With diethylmalonyl chloride retene yields diethylreteneindandione, $C_{25}H_{26}O_2$, m.p. 134-135°.[436]

According to Perrier,[437] the compound obtained by heating benzoyl chloride with aluminum chloride in carbon disulfide solution reacts with retene to form an acylated product, $(C_6H_5COC_{18}H_{17})_2Al_2Cl_6$.

The condensation of pyrene with alkyaryl carbamyl halides in the presence of anhydrous aluminum chloride has been claimed to yield alkylarylcarbamyl pyrenes which may be hydrolyzed to give a pyrene carboxylic acid.[438] Thus pyrene may be heated in chlorobenzene in the

[430] L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, 60, 1658-1665 (1938).
[431] D. E. Adelson and M. T. Bogert, *J. Am. Chem. Soc.*, 58, 853-854 (1936). M. T. Bogert and T. Hasselstrom, *J. Am. Chem. Soc.*, 53, 3462-3466 (1931). *cf.* G. Komppa and E. Wahlforss, *J. Am. Chem. Soc.*, 52, 5009-5017 (1930); G. A. Nyman, *Ann. Acad. Sci. Fennicae*, A48, No. 6, 32 pp. (1937); *C. A.*, 33, 8192.
[432] W. P. Campbell and D. Todd, *J. Am. Chem. Soc.*, 62, 1287-1292 (1940).
[433] U. S. P. 2,054,107 (1936) to E. Wahlforss and L. A. Goldblatt (to Glidden Co.); *C. A.*, 30, 7569.
[434] G. A. Nyman, *Ann. Acad. Sci. Fennicae*, A41, No. 5, 30 pp. (1934); *C. A.*, 30, 2958.
[435] C. Liebermann, *Ber.*, 44, 850-858 (1911).
[436] M. Freund and K. Fleischer, *Ann.*, 373, 291-336 (1910); *J. Chem. Soc. Abs.*, 98 (I), 490 (1910).
[437] G. Perrier, *Compt. rend.*, 116, 1293 (1893).
[438] British P. 486,868 (1938) to George Sheldrick, Max Wyer, and Imperial Chemical Industries Ltd.; *C. A.*, 32, 8441. See also British P. 510,901 to I. G. Farbenind., *C. A.*, 34, 5467, for the preparation of carboxylic acids by reaction of compounds having at least 4 rings with phosgene and aluminum chloride.

presence of aluminum chloride with ethylphenylcarbamyl chloride to give 3-ethylphenylcarbamylpyrene which, upon boiling with sulfuric acid, gives pyrene-3-carboxylic acid according to the equations:



Dicarboxylic derivatives may be secured by using 2 moles of the carbamyl chlorides.

The acetylation of pyrene yields 3-acetylpyrene, m.p. 94°.[439] Dziewonski and Sternbach [440] used pyrene and acetyl chloride in nitrobenzene in the presence of aluminum chloride at 20° for this reaction. Similarly, from 40 g of pyrene and 35 cc of propionyl chloride, 42 g of 3-propionylpyrene (m.p. 84-85°) has been obtained.[441] By Friedel-Crafts condensation of 2 moles of chloroacetyl chloride with pyrene, a mixture of two isomeric diacetyl derivatives, 3,8-dichloroacetyl- and 3,10-dichloroacetylpyrene, is obtained.[442]

Pyrene has been reported to react with benzoyl chloride with aluminum chloride and carbon disulfide to give 3-benzoylpyrene if one mole of the acid chloride is used, or a mixture of di- and tribenzoylpyrenes if 2 moles of benzoyl chloride are used.[443] However, Vollmann and co-workers [444] have found that only a mixture of 3,8- and 3,10-dibenzoylpyrenes is produced by this reaction. A tri-acylated compound could not be isolated. 3-Benzoylpyrene (m.p. 128°) was prepared in excellent yield by these workers if nitrobenzene instead of carbon disulfide was used as solvent.

With α-naphthoyl chloride, a mixture of 3,8- and 3,10-di-α-naphthoylpyrenes is obtained. Use of β-naphthoyl chloride gives the corresponding β-derivative.[443]

Scholl, Meyer and Donat,[445] however, report that replacement of carbon disulfide by benzene, toluene, chlorobenzene, or tetrachloroethane and avoidance of a temperature greater than 20° leads to a great improvement in the yield of 3-aroylpyrenes obtained from aroyl chlorides, pyrene and aluminum chloride.

[439] K. Dziewonski and L. Sternbach, *Bull. intern. acad. polonaise sci.*, 1937, A, 81-85; *Brit. Chem. Abstracts-A*, 285 (1937) (II).
[440] K. Dziewonski and L. Sternbach. *Roczniki Chem.*, 17, 101-104 (1937); *Brit. Chem. Abstracts-A*, 248 (1937) (II).
[441] K. Dziewonski and P. Trzesinski, *Bull. intern. acad. polonaise sci. Classe sci. math. nat.*, 1937 A, 579-582 (in German); *C. A.*, 32, 4978.
[442] H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Ann.*, 531, 1-159 (1937).
[443] R. Scholl and C. Seer, *Ann.*, 394, 111-177 (1912).
[444] H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Ann.*, 531, 1-159 (1937).
[445] R. Scholl, K. Meyer, and J. Donat, *Ber.*, 70, 2180-2189 (1937); *Brit. Chem. Abs.-A* (II), 20 (1938).

The following 3-aroylpyrenes have been prepared by these authors using the corresponding hydrocarbon and aroyl chloride with aluminum chloride and the indicated solvent:

Ketone	m.p.	Solvent	Yield (%)
3-Benzoylpyrene	128-129°	*sym*-tetrachloroethane	90
3-*p*-Bromobenzoylpyrene	174-175°	benzene	90
3-*p*-Toluylpyrene	155-156°	benzene	..
3-Cinnamylpyrene	119.5-120.5°	benzene	..
3-α-Naphthoylpyrene	153-154°	benzene	80

The procedure given above for the preparation of these compounds as well as of *p*-bromobenzoylpyrene (m.p. 174-175°), β-naphthoylpyrene (m.p. 150-151°) and *o*-chlorobenzoylpyrene (m.p. 151.5-152.5°) has been patented.[447]

Ketones produced by the aluminum chloride condensation of pyrene with aromatic carboxylic acid chlorides such as benzoyl chloride, *m*-chlorobenzoyl chloride, *p*-toluyl chloride or α-naphthoyl chloride are also claimed in a patent to General Aniline Works[448] as intermediate compounds in the production of vat dyes.

In addition to this, another patent[449] also recommends the use of such solvents as benzene, toluene, chlorobenzene or tetrachlorethane for the production of ketones of the pyrene series by the interaction of pyrene with halides of α- and β-unsaturated or aromatic acids having at least one free *o*-position. For example, an 80 per cent theoretical yield of monobenzoylpyrene (m.p. 124°) was obtained by shaking 10 parts of pyrene in 80 parts of benzene with 9.1 parts of benzoyl chloride and 7 parts of aluminum chloride at 20° for five hours.

Acyl derivatives of benzopyrenes have been prepared. Thus by reacting 3,4-benzopyrene with acetyl chloride in the presence of aluminum chloride in carbon disulfide, a 66 per cent yield of 10-acetyl-3,4-benzopyrene was secured.[450]

Perylene and chloroacetyl chloride give 3,9-dichloroacetylperylene with aluminum chloride in carbon disulfide.[451]

By allowing a mixture of ethylchrysene, acetyl chloride, aluminum chloride and carbon disulfide to stand for twelve hours, and then heating for five hours, acetyl-2-ethylchrysene (m.p. 131°) has been prepared.[452]

Work has been done on the acylation of dichloroperylenes. A patent to F. Bensa[453] claims the production of 3,9-dichloro-4,10-diacetyl- (or dipropionyl-) perylene from 3,9-dichloroperylene, aluminum chloride in carbon disulfide, and acetyl- or propionylchloride. Both compounds may be obtained by crystallization from nitrobenzene or xylene; they do not melt without decomposition.

[447] U. S. P. 2,069,653 (1937) to R. Schöll, K. Meyer and J. Donat, *C. A.*, **31**, 1231.
[448] U. S. P. 2,023,536 to Georg Kranzlein, Heinrich Vollmann, and W. Schultheis (to General Aniline Works), *C. A.*, **30**, 875.
[449] British P. 462,209 (1936) to Soc. Chem. Ind. in Basle; *Brit. Chem. Abs.*-B, 551 (1937).
[450] A. Windaus and K. Raichle, *Ann.*, **537**, 157-70 (1939); *C. A.*, **33**, 2123.
[451] A. Zinke, O. Benndorf, and H. Kolmayr, *Monatsh.*, **56**, 152-162; *Brit. Chem. Abs.*-A, 1587 (1930); 421.
[452] K. Funke and J. Rutte, *J. prakt. Chem.*, **146**, 151-158 (1936); *Chem. Zentr.*, 1936, II.
[453] British P. 278,325 (1927) to F. Bensa, *Brit. Chem. Abs.*-B, 199 (1928); *C. Z.*, 1928, I 851.

Pongratz [454] secured 3,9-dichloroperylene-4,10-dibutyrylperylene (m.p. 258-259°) by the Friedel-Crafts reaction from 3,9-dichloroperylene and butyryl chloride.

Reacting 2 moles of benzoyl chloride with 1 mole of perylene and aluminum chloride in carbon disulfide results in the formation of dibenzoylperylene.[455] This was later identified as 3,9-dibenzoyl perylene.[456] When benzoyl chloride was reacted with perylene in the presence of aluminum chloride, and the reaction mixture was allowed to stand for twenty to forty hours at room temperature, Zinke and Benndorf [457] obtained a mixture of 3,9- and 3,4-dibenzoylperylene. By suspending perylene in 4-chlorobenzoyl chloride and treating it, under cooling, with aluminum chloride, 3,4-bis(4-chlorobenzoyl)perylene (m.p. 346-347°), together with a small amount of the corresponding 3,9-compound, was prepared.[458]

Pongratz and Halabarda [459] also report the formation of a diketone; from perylene and *m*-toluyl chloride with aluminum chloride they obtained di-*m*-toluylperylene, m.p. 245-250°. With *p*-toluyl chloride, 3,9-di-*p*-toluylperylene [m.p. 317-318.5° (corr.)], was secured.[458]

Benzoyl chloride was reacted with 3,9-dibromoperylene by Zinke and co-workers.[460] They allowed to stand overnight a mixture consisting of 1 g of the halogenated perylene, 24 cc of carbon disulfide, 0.8 g of benzoyl chloride and 1 g of aluminum chloride. The mixture was subsequently boiled for three hours and then subjected to customary treatment for isolation of the ketone. The product obtained was 4,10-dibenzoyl-3,9-dibromoperylene, m.p. 355° (with decomposition). In the same way, 4,10-dibenzoyl-3,9-dichloroperylene was secured from 3,9-dichloroperylene and benzoyl chloride.[461]

Zinke and co-workers [462] have also reacted 4,10-dichloroperylene with *p*-chlorobenzoyl chloride in the presence of aluminum chloride. The reactants, in carbon disulfide, were allowed to stand for 24 hours; the mixture was then refluxed for two hours. 3,9-Di-*p*-chlorobenzoyl-4,10-dichloroperylene (m.p. about 350°) was obtained. In the same way, using *p*-bromobenzoyl chloride instead of *p*-chlorobenzoyl chloride, was obtained 3,9-bis(*p*-bromobenzoyl)-4,10-dichloroperylene, m.p. about 370°.

Using substantially the same procedure, 4,10-dichloroperylene was reacted with other aroyl chlorides and the following products were obtained:

3,9-di-*o*-toluyl-4,10-dichloroperylene, m.p. 351°
3,9-di-*m*-toluyl-4,10-dichloroperylene, m.p. 334°
3,9-di-*p*-toluyl-4,10-dichloroperylene, m.p. 345°
3-*α*-naphthoyl-4,10-dichloroperylene, m.p. 275°
3-*β*-naphthoyl-4,10-dichloroperylene, m.p. 293°

[454] A. Pongratz, *Monatsh.*, 50, 87-96; *C. A.*, 23, 1130 (1929).
[455] R. Scholl, C. Seer, and R. Weitsenbock, *Ber.*, 43, 2202-2209 (1910).
[456] A. Zinke, F. Linner, and D. Wolfbauer, *Ber.*, 58, 323 (1925).
[457] A. Zinke and O. Benndorf, *Monatsh.*, 56, 153-162 (1930); *C. A.*, 25, 293.
[458] A. Pongratz and G. Markgraf, *Monatsh.*, 66, 178-180 (1935); *C. A.*, 29, 7978.
[459] A. Pongratz and A. Halabarda, *Monatsh.*, 56, 163-178 (1930); *C. A.*, 25, 292.
[460] A. Zinke, F. Linner, and O. Wolfbauer, *Ber.*, 58, 329 (1925).
[461] A. Zinke, A. Pongratz, and K. Funke, *Ber.*, 58, 331 (1925).
[462] A. Zinke, K. Funke, and A. Pongratz, *Ber.*, 58, 799-802 (1925); *J. Chem. Soc. Abs.*, 128 (I), 810 (1925).

It is of interest that in the reaction of dichloroperylene with α- or β-naphthoyl chlorides, only mono-substitution is obtained. In the other acylations of perylene, in spite of the fact that an excess of the acyl chloride was not used, di-substitution had invariably resulted.

Reaction of 2,3,10,11-dinaphthoperylene and benzoyl chloride with aluminum chloride and carbon disulfide results in the formation of a tribenzoylnaphthoperylene.[463]

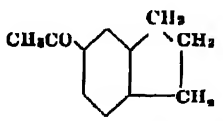
The condensation of chrysene and benzoyl chloride with aluminum chloride in carbon disulfide gives a good yield of 2-benzoylchrysene, m.p 191°.[464] The preparation of 2-benzoylchrysene (m.p. 186-187°) from chrysene and benzoyl chloride in the presence of aluminum chloride has been patented.[465] Excess of benzoyl chloride with chrysene and aluminum chloride, allowed to stand for 48 hours at room temperature and then warmed for one hour at 100°, gives two dibenzoylchrysenes, m.p 208 and 252°. Ethylchrysene and benzoyl chloride with aluminum chloride in carbon disulfide give a benzoylethylchrysene, m.p. 130°.[466]

The condensation of polynuclear hydrocarbons with highly aromatic carboxylic chlorides results in the formation of various dyes or dye intermediates. In a du Pont patent,[467] dibenzanthrone derivatives having 2,2'-positions free are condensed in the presence of aluminum chloride with carboxylic chlorides such as, for example, 1-chloroanthraquinone-2-carboxylyl chloride for the manufacture of vat dyes.

Partially Saturated Cyclic Hydrocarbons *

Since the cycloaliphatic hydrocarbons resemble aliphatic hydrocarbons in Friedel-Crafts reaction, a discussion of condensations effected with members of the cycloaliphatic series is found in the chapter devoted to Friedel-Crafts reactions in aliphatic chemistry.

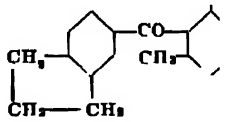
The reaction of hydrindene with acid chlorides was studied by von Braun and co-workers.[468] They added, with ice-cooling, 12 g of aluminum chloride to a mixture of 10 g of hydrindene, 7 g of acetyl chloride and 50 g of carbon disulfide. After letting stand for two hours, the reaction mass was decomposed with ice. Customary distillation and purification gave a product, b.p. 134-135°/11 mm, which was identified as β-hydrindyl methyl ketone,



[463] B. Schiedt, *Ber.*, 71, 1248-1253 (1938).
[464] K. Funke and E. Müller, *J. prakt. Chem.*, 144, 242-250 (1936); *C. A.*, 30, 2957 (1936)
[465] German P. 652,912 (1937) to H. Vollmann and H. Becker (to I. G. Farbenindustrie), *Zentr.*, 1938, I, 2064.
[466] K. Funke and J. Rathe, *J. prakt. Chem.*, 146, 151-158 (1936); *C. A.*, 30, 8206
[467] U. S. P. 2,051,121 (1936) to A. J. Wuertz (to du Pont), *C. A.*, 30, 6959. See also French P. 841,096 to Soc. pour l'ind. chim. a Bale; *C. A.*, 34, 1863
* See under naphthalene and anthracene for acylation of partially hydrogenated naphthalenes and anthracenes.
[468] J. von Braun, G. Kirschbaum, and H. Schumann, *Ber.*, 53, 1155-1173 (1920).

the acetylation occurring in the 6-position. The yield was 90 per cent of theoretical. The preparation was repeated by Borsche and Pommer,[469] who gave 267-268°/748 mm as the boiling point of the acetylhydrindene obtained. The latter also found that the reaction of benzoyl chloride with hydrindene proceeded similarly, giving benzoylhydrindene, melting indefinitely above 40°.

In his work on cancer-producing hydrocarbons, Cook[470] reacted hydrindene with 2-methyl-1-naphthoyl chloride by gradual addition of 1 part of aluminum chloride to an ice-cold mixture of 1 part of the acid chloride, 1 part of the hydrocarbon, and 3 parts of carbon disulfide. He secured a ketone probably having the structure



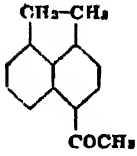
which could not be isolated. Later, Cook[471] showed that when this ketone was heated at 450° for two hours, 5,6-cyclopenteno-1,2-benzanthracene (m.p. 199-200°) was formed.

Julius von Braun[468] studied the reaction of oxalyl chloride on hydrindene. Since in the Friedel-Crafts reaction oxalyl chloride may be decomposed under the action of the catalyst to yield phosgene and carbon monoxide, carboxylation occurs in the reaction of oxalyl chloride with hydrindene, the product being β-hydrindene carboxylic acid (in about 60 per cent of theoretical yield) together with a small amount of the α-isomer.

Indene polymerizes in the presence of aluminum chloride; simultaneous polymerization and acylation with higher aliphatic acid halides has been claimed to give resins having unusual properties.[472]

Acenaphthene was acetylated by Graebe and Haas.[473] Ten parts of acenaphthene, 70-80 parts of carbon disulfide and about 7 parts of acetyl chloride were heated under reflux on a water-bath; then gradually 10 parts of aluminum chloride was added, the entire operation lasting from 1 to 1½ hours. After usual decomposition of catalyst and removal of solvent, the acetylacenaphthene was distilled off at 350-360°. Upon crystallization from alcohol, the pure compound was found to melt at 75° and boil at 361°. Graebe calls it 4-acetylacenaphthene, but the structure which he assigned to it,

[469] W. Borsche and M. Pommer, *Ber.*, **54**, 102-110 (1921).
[470] J. W. Cook, *J. Chem. Soc.*, 499-507 (1931).
[471] J. W. Cook, *J. Chem. Soc.*, 1931, 2529-2532; *Brit. Chem. Abs.*-A, 1407 (1931).
[472] U. S. P. 2,197,710 (1940) to A. W. Ralston, R. J Vander Wal, and S. T. Bauer (to Armour and Co.).
[473] C. Graebe and P. Haas, *Ann.*, **327**, 91-99 (1903).



corresponds to what would now be designated as the 3-acetylacenaphthene.

More recently, Fieser and Hershberg [474] isolated, through the picrate, from the product resulting from the reaction of acenaphthene with acetyl chloride and aluminum chloride in nitrobenzene solution pure 3-acetylacenaphthene, existing in two interconvertible polymorphic forms melting at 57° and 70°. From the mother liquor there was obtained a small amount of colorless prisms of 1-acetylacenaphthene, m.p. 103.5-104.5°. It is probable that Graebe's 3-acetylacenaphthene, purified only by distillation and crystallization, was really a mixture of the two isomers.

In preparing large amounts of 3-acetylacenaphthene according to Graebe's method, Fleischer and Wolff [475] obtained from the high-boiling fractions of the product a diacetylacenaphthene, m.p. 146°. An I. G. patent [476] claims the production of a diacetylacenaphthene, also melting at 146°, by dissolving the mono-acetylacenaphthene in carbon disulfide, adding aluminum chloride, and then, under stirring, a solution of acetyl chloride and more aluminum chloride in carbon disulfide. The amount of diacetyl compound obtained is said to be 70-80 per cent of the theoretical

Friedel-Crafts reaction of β-chloropropionyl chloride with acenaphthene yields 3-(β-chloropropionyl)acenaphthene.[477]

Mayer and Kaufmann [478] obtained 3-chloroacetylacenaphthene (m.p. 104°) by slowly treating with 30 g of aluminum chloride a solution of 25 g of acenaphthene and 30 g of chloroacetyl chloride in 250 cc of boiling carbon disulfide. The corresponding bromo- compound (m.p. 180°) and an unidentified substance (m.p. 94-96°) were obtained from acenaphthene and bromoacetyl chloride in the presence of aluminum chloride by Fleischer and Wolff.[475] Dichloroacetylacenaphthene (m.p. 194-195°) is claimed in an I. G. patent [479] as the product of the reaction of acenaphthene and excess amounts of chloroacetyl chloride and aluminum chloride.

When Fleischer and Wolff [475] treated 3-ethylacenaphthene with acetyl chloride and aluminum chloride they obtained the 4-(?)-acetyl derivative, m.p. 110-5°.

Acenaphthene in carbon disulfide was reacted with propionyl chloride in the presence of aluminum chloride by Dziewonski and Moszew.[480] They

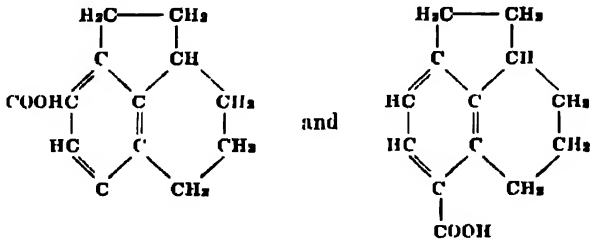
[474] L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, 61, 1272-1281 (1939).
[475] K. Fleischer and P. Wolff, *Ber.*, 53, 925-931 (1920); *J. Chem. Soc. Abs.*, 118 (I), 540 (1920); *C. A.*, 14, 3249.
[476] British P. 279,506 (1927) and French P. 642,907 (1928) to I. G. Farbenindustrie; *Chem. Zentr.* 1929, I, 2237.
[477] F. Mayer and P. Müller, *Ber.*, 60, 2278-2288 (1927).
[478] F. Mayer and W. Kaufmann, *Ber.*, 53, 289-296 (1920); *J. Chem. Soc. Abs.*, 118 (I), 801 (1920).
[479] French P. 642,907 (1928) and British P. 279,506 (1927) to I. G. Farbenindustrie; *C. Z.*, 1929, I, 2237.
[480] K. Dziewonski and J. Moszew, *Rocz. Chem.*, 11, 415-425 (1931); *Brit. Chem. Abs.*-A, 959 (1931).

obtained 3-propionylacenaphthene (m.p. 69.5-70°) and a second ketone, 3,4-dipropionylacenaphthene, m.p. 122-123°.

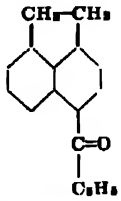
Condensation of crotonyl chloride with acenaphthene and aluminum chloride in carbon disulfide solution gives a 43 per cent yield of 3-crotonylacenaphthene.[481]

Dimethylmalonyl chloride reacts with acenaphthene in carbon disulfide with aluminum chloride to give two indandiones, 5,6-acenaphthenedimethylindandione (m.p. 127.5-129°) and isoacenaphthenedimethylindandione, m.p. 176.5-177.5°.[482] Diethylmalonyl chloride has been reacted with acenaphthene by Freund and Fleischer.[483] They obtained 5,6-acenaphthenediethylindandione (m.p. 156°), another acenaphthenediethylindandione (m.p. 109-111°), and diethyldiacenaphthoylmethane, m.p. 229-231°.

Oxalyl chloride with tetrahydroacenaphthene and aluminum chloride results in carboxylation, a mixture of two isomeric tetrahydroacenaphthene carboxylic acids being obtained[484]:



The reaction of acenaphthene with benzoyl chloride was reported by Graebe and Haas.[485] They dissolved 20 g of acenaphthene and 28 g benzoyl chloride in about 150 cc of carbon disulfide, added 20 g of aluminum chloride, and heated under reflux for 1½ hours. After usual decomposition of complex, removal of solvent and distillation, they obtained from the fraction b. 380-410°, by crystallization, from alcohol or acetic acid, a benzoylacenaphthene, m.p. 101°. This was called 4-benzoylacenaphthene; but according to the structure which they assigned to it, the benzoyl substitution was in what is now termed the 3-position:



[481] I. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **61**, 1272-1281 (1939).
[482] M. Fruend and K. Fleischer, *Ann.*, **399**, 182-241 (1913), *C. A.*, **7**, 3737.
[483] M. Freund and K. Fleischer, *Ann.*, **373**, 291-336 (1910); *J. Chem. Soc. Abs.*, **98** (I), 490 (1910); *Ann.*, **402**, 51-76 (1914).
[484] J. v. Braun, G. Kirschbaum, and H. Schuhmann, *Ber.*, **53**, 1155-1173 (1920).
[485] C. Graebe and P. Haas, *Ann.*, **327**, 96 (1903).

Using essentially the same method, Dziewonski and Rychlik [486] obtained a 60-70 per cent yield of 3-benzoylacenaphthene, m.p. 100-101°. A 77 per cent yield [487] is obtained when nitrobenzene is used as solvent.

Recently, Bowden and Harris [488] report that by modifying the procedure of Graebe and Haas, they obtained a very pure product, to which they gave the same structure. These workers, however, report the m.p. to be 85°.

Benzoylacenaphthene was also prepared by Perrier,[489] who reacted the addition product, $C_6H_5COCl.AlCl_3$, with acenaphthene in carbon disulfide solution. When acenaphthene and *o*-toluyl chloride are condensed with aluminum chloride in carbon disulfide, substitution occurs in the 3-position, giving a 23 per cent yield of 3-*o*-toluylacenaphthene, m.p. 139-140°.[490] Acenaphthene has also been reacted with 2-methyl-1-naphthoyl chloride, a 65 per cent yield of 3-(2′-methyl-1′-naphthoyl)acenaphthene being secured.[491]

Fluorene was condensed with acetyl chloride in the presence of aluminum chloride in carbon disulfide solution by Dziewonski and Schnayder.[492] They obtained 2-acetylfluorene, m.p. 132°, and the diketone, 2,7-diacetylfluorene, m.p. 182-184°. In the similarly performed condensation of 2-benzylfluorene with acetyl chloride, Dziewonski and co-workers [493] obtained 7-acetyl-2-benzylfluorene, m.p. 130-131°.

The reaction of fluorene with acetyl chloride was studied more carefully by Dziewonski and Kleszcz [494] who found that, whereas at 5-10° the main reaction product was 2-acetylfluorene, if temperatures of 20-25° were used, diacetylation occurred. According to Rieveschl and Ray [495] the diacetylated fluorene thus obtained is 2,3-diacetylfluorene.

With dimethylmalonyl chloride, fluorene gives two isomeric dimethylmalonylfluorenes. Freund and co-workers [496] dissolved 0.2 mole of fluorene in 200 cc of carbon disulfide and added 0.3 mole of dimethylmalonyl chloride. To this, during a half hour, 70 g of aluminum chloride was added. The reaction mixture was then gently heated for 1½ hours decomposed with ice and then distilled. By repeated crystallization from benzene 11 g of α-fluorenedimethylindandione (m.p. 220-221°) and 15 g of the β-isomer (m.p. 156-158°) were obtained. The structure of these compounds could not be determined satisfactorily, and they have simply been designated as the α- and β-compounds. There was also obtained 1.5 g of isobutyrylfluorene, m.p. 80-82°. The latter was no doubt formed by the conversion of dimethylmalonyl chloride into isobutyryl chloride and the reaction of the latter on the fluorene.

[486] K. Dziewonski and M. Rychlik, *Ber.*, **58**, 2239-2249 (1925).
[487] E. J. Chu, *J. Chinese Chem. Soc.*, **7**, 14-19 (1939); *C. A.*, **34**, 1987.
[488] S. T. Bowden and W. E. Harris, *J. Chem. Soc.*, 307-310 (1939).
[489] G. Perrier, *Bull. soc. chim. (3)*, **31**, 859-862 (1904).
[490] B. P. Geyer and S. Zuffanti, *J. Am. Chem. Soc.*, **57**, 1787-1788 (1935); *C. A.*, **29**, 7971.
[491] J. W. Cook, *J. Chem. Soc.*, 499-507 (1931).
[492] K. Dziewonski and J. Schnayder, *Bull. intern. acad. polonaise sci.*, 1930 A, 529-535; *Brit. Chem. Abs.-A*, 622 (1931).
[493] K. Dziewonski, M. Dominikowna, L. Gaus'kowna, and L. Mus, *Roczniki Chem.*, **13**, 283-292 (1933); *Brit. Chem. Abs.-A*, 826 (1933).
[494] K. Dziewonski and Kleszcz, *Roczniki Chem.*, **12**, 187 (1932); *C. A.*, **27**, 283.
[495] G. Rieveschl and F. E. Ray, *Chem. Reviews*, **23**, 365 (1938).
[496] M. Freund, K. Fleischer, and J. Stemmer, *Ann.*, **414**, 44-58 (1917).

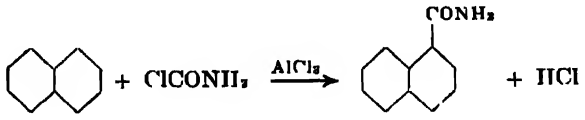
Fortner [497] condensed fluorene with benzoyl chloride with aluminum chloride in carbon disulfide solution and obtained 2-benzoylfluorene, m.p. 124-126°. Dziewonski and Obtulowicz also reported that fluorene and benzoyl chloride with aluminum chloride in carbon disulfide at ordinary temperature gave 2-benzoylfluorene, m.p. 122°. When benzylfluorene was condensed with benzoyl chloride, the acyl group went into the 7-position, resulting in the symmetrically substituted fluorene.[498] The resulting 7-benzoyl-2-benzylfluorene melts at 126-127° and boils at 340-350°/15 mm.

The 7-position was also taken in the condensation of 2-benzoylfluorene with benzoyl chloride and aluminum chloride in carbon disulfide under heating. The 2,7-dibenzoylfluorene so prepared melts at 193-194°. By reacting fluorene with 2-methyl-1-naphthoyl chloride, an 85 per cent yield of 2-(2'-methyl-1'-naphthoyl)fluorene (m.p. 169-170°) was secured.

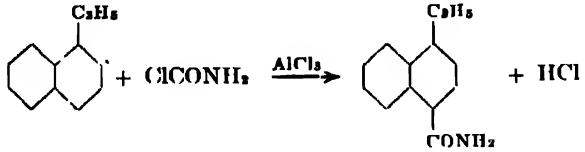
2-Benzoylfluorene has also been prepared by Perrier,[499] who secured a purer compound by first allowing the benzoyl chloride to react with the aluminum chloride and then adding the fluorene.

Polynuclear Hydrocarbons and Nitrogenous Acid Chlorides

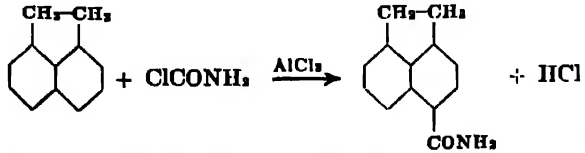
According to Gattermann,[500] carbamyl chloride or N-alkylcarbamyl chlorides condense with polynuclear hydrocarbons in the presence of aluminum chloride in carbon disulfide to give monocarboxylic amides of the hydrocarbon employed. Thus naphthalene and carbamyl chloride give α-naphthoic acid amide (m.p. 202°) according to the equation:



With α-ethylnaphthalene, *para*-substitution is secured:



Acenaphthene reacts similarly:



[497] M. Fortner, *Monatsh.*, **23**, 921-938 (1902); *J. Chem. Soc. Abs.*, **84** (I), 177 (1903); *Monatsh.*, **25**, 443 (1904); *J. Chem. Soc. Abs.*, **86** (I), 739 (1904).
[498] K. Dziewonski, M. Dominikowna, L. Gauszkowna, and L. Mus, *Rocznik Chem.*, **13**, 283-292 (1933); *Brit. Chem. Abs.-A*, 826 (1933).
[499] G. Perrier, *Monatsh.*, **24**, 591 (1903).
[500] L. Gattermann, *Ann.*, **244**, 29-78 (1888).

The preparation of pyrene carboxylic acid by reacting pyrene with carbamyl chloride in the presence of aluminum chloride and saponifying the amide obtained has been patented.[501]

The preparation of high molecular aromatic carboxylic acid amides by the action of up to 2 molecules of carbamyl chloride or its alkyl, aralkyl or aryl derivatives on one molecule of an aromatic hydrocarbon with at least three condensed benzene rings, or on one molecule of a non-basic reacting heterocyclic compound with at least two condensed benzene rings or on their halogen substitution products, has been patented.[502]

The reaction products of N-methylcarbamyl chloride with the following compounds are described:

3-chloropyrene
3-methylpyrene
4-methylpyrene
perylene
naphthofluorene
isochrysofluorene
1,2-benzanthracene
naphthacene
picene

Reaction products of carbamyl chloride with the following are also prepared:

fluoranthrene
triphenylene
bascane

Although the reaction of carbamyl chloride with benzene or benzene homologs has long been known, the instability of carbamyl chloride has occasioned difficulty in its use. In 1936, however, Hopff and Ohlinger[503] found that carbamyl chloride or its alkyl substitution products are stabilized by treatment with Friedel-Crafts type catalysts. Carbon disulfide is mixed with carbamyl chloride and anhydrous aluminum chloride is added in small amounts. The carbon disulfide is distilled off by gentle heating, leaving the acid chloride in a readily powdered stable condition.

The use of the carbamyl chloride-aluminum chloride condensation product greatly facilitates the Friedel-Crafts reaction with aromatic hydrocarbons. Thus, in the preparation of 4,4'-biphenyl dicarboxylic acid amide, one molecular proportion of diphenyl is caused to react with two molecular proportions of the compound derived from 37.5 per cent of carbamyl chloride and 62.5 per cent of aluminum chloride obtained as described above. Commercial dichlorobenzene is used as solvent, and

[501] Swiss P. 180,716 (1937) to Soc. pour l'ind. chim. a Bale; *C. A.*, 32, 800.

[502] German P. 650,802 (1937) to H. Hopff and H. Ohlinger (to I. G.); *C. A.*, 32, 505. British P. 448,788 (1934) to I. G.; *Brit. Chem. Abs.*-B, 875 (1936). French P. 797,072 (1936) to I. G.; *C. A.*, 30, 6280.

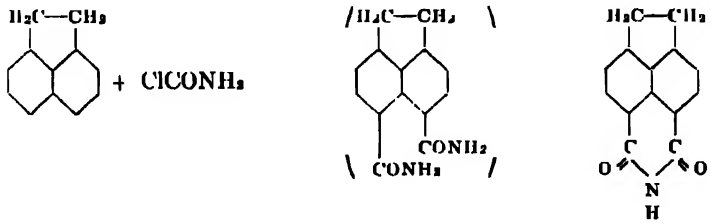
[503] U. S. P. 2,052,128 (1936) to H. Hopff and H. Ohlinger (to I. G.); *C. A.*, 30, 6762. German P. 630,936 (1936); *C. A.*, 31, 3943. Brit. P. 449,100 (1936); *C. A.*, 30, 7598. French P. 797,771 (1936); *C. A.*, 30, 7292; all to I. G. Farbenindustrie.

the reaction mixture is heated while gradually raising the temperature from 60° to 140° until hydrogen chloride has ceased to be evolved.[504]

Other polynuclear aromatic hydrocarbons react similarly, the following dicarboxylic acid amides having been formed by the process:

fluorene dicarboxylic acid diamide, m.p. 292°
stilbene dicarboxylic acid diamide, m.p. 322-323°
chrysene dicarboxylic acid diamide
pyrene dicarboxylic acid diamide
fluoranthrene dicarboxylic acid diamide

If the two carboxylic amido- groups enter into the *peri*-position of the hydrocarbon, dicarboxylic imides are secured instead of diamides. For example, acenaphthene-5,6-dicarboxylic imide is secured in good yield from acenaphthene:



Reactants which yield carbamyl chloride may be used for the production of aromatic amides. Cyanic acid with hydrogen chloride in the presence of aluminum chloride reacts with naphthalene to give α-naphthamide.[505] A mixture of potassium cyanate, naphthalene, and aluminum chloride similarly gives α-naphthamide.[506]

Acenaphthene amide (m.p. 197-198°) is easily obtained by reaction of cyanic acid, hydrogen chloride, and acenaphthene under the influence of aluminum chloride.[505]

Polycyclic aromatic hydrocarbons may be condensed with alkylarylcarbamyl chlorides to give alkyl anilides of aromatic carboxylic acids.[507] Condensation proceeds in the presence of aluminum chloride, the reaction being similar to that of aromatic hydrocarbons with carbamyl chloride or with alkylcarbamyl chlorides. For example, from acenaphthene and phenylethylcarbamyl chloride there is obtained acenaphthene-5-carboxylic acid ethylanilide (m.p. 158°) or acenaphthene-5,6-dicarboxylic acid ethylanilide, m.p. 217°.

Cyanoacetyl chloride condenses with polynuclear hydrocarbons to give normal Friedel-Crafts substitution. With 1-methylnaphthalene and

[504] U. S. P. 2,137,287 (1938) to H. Hopff and H. Ohlinger. Brit. P. 456,070 (1935) to I. G. Farbenindustrie; *Brit. Chem. Abs.*-B, 130 (1937). French P. 803,257 (1936) to I. G.; *C. A.*, 31, 2615.
[505] L. Gattermann and A. Rossolymo, *Ber.*, 23, 1199-1199; *J. Chem. Soc. Abs.*, 58 (II), 974-5 (1890).
[506] German P. 584,142 (1933) to H. Hopff (to I. G. Farbenindustrie); *C. A.*, 28, 174.
[507] U. S. P. 2,072,227 (1937) to M. Wyler and A. Kershaw (to Imperial Chemical Industries, Ltd.); *C. A.*, 31, 2615. French P. 783,061 (1935) to Imperial Chemical Industries; *C. Z.*, 1935, II, 2480. Brit. P. 489,618 (1938) to G. Sheldricks and M. Wyler (to Imperial Chemical Industries, Ltd.); *C. A.*, 33, 645.

cyanoacetyl chloride in the presence of aluminum chloride and a solvent at below 60°, there is obtained a cyanoacetyl-1-methylnaphthalene (m.p. 127°) according to the reaction:

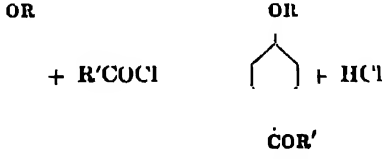
$$C_6H_4.CH_2 + NC.CH_2COCl \xrightarrow{AlCl_3} NC.CH_2CO.C_6H_3.CH_3 + HCl$$

Acenaphthene reacts similarly to give 5-cyanoacetylacenaphthene.[508]

Reaction of Ethers with Acyl Chlorides

Unsubstituted Phenol Ethers and Acyl Chlorides

Anisole. Alkyl ethers of phenol react with acid chlorides in the presence of aluminum chloride to give *p*-acyl substitution:

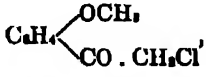


The reaction of anisole with acetyl chloride has been much studied.[509] Baranger [509] reports that *p*-acylanisoles were obtained in excellent yields by slowly dropping the acid chloride into a solution of anisole in carbon disulfide in the presence of anhydrous aluminum chloride. Thus a 96 per cent yield of *p*-acetylanisole (m.p. 38-39°) was secured by using 200 g of acetyl chloride, 200 g of anisole, 300 g of anhydrous aluminum chloride and 500 g of anhydrous carbon disulfide.

Gattermann and co-workers [505] dissolved anisole and acetyl chloride in carbon disulfide and gradually added aluminum chloride. Besides *p*-acetylanisole, they also obtained dianisylethylene, $C_2H_2(C_6H_4.OCH_3)_2$.

No solvent was used by Kuroda and Matsukuma.[509] With an excess of acetyl chloride, they secured only a 35 per cent of theoretical yield of *p*-acetylanisole, together with considerable quantities of a crystalline substance melting at 135°. In view of the fact that when this method was applied to other acetylations it gave theoretical yields, the low yield obtained here is noteworthy, and corresponds to Gattermann's experience.

Disubstitution has been reported in the reaction of chloroacetyl chloride with anisole. By adding 22.5 g of anhydrous aluminum chloride to 15 g of anisole and 22.5 g of chloroacetyl chloride in carbon disulfide, Kunckell and Johannssen [510] obtained *p*-(chloroacetyl)anisole



[504] British P. 342,373 (1929) to I. G. Farbenindustrie; *Brit. Chem. Abs.*-B, 476 (1931).
[505] P. M. Baranger, *Bull. soc. chim.*, 49, 1218-1222 (1931). L. Gattermann, R. Ehrhardt, and H. Mauch, *Ber.*, 22, 1129-1133 (1889); *Ber.*, 23, 1199-1210 (1890). C. Kuroda and T. Matsukuma, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 18, 51-60 (1932); *Brit. Chem. Abs.*-A, 388 (1932). A. F. Holleman, *Rec. trav. chim.*, 10, 215 (1891). J. F. Eijkman, F. Bergema, and J. T. Henriard, *Weekblad*, 2, 59-72, 79-99; *C. Z.*, 1905, I, 814.
[506] F. Kunckell and F. Johannssen, *Ber.*, 30, 1714-1716 (1897); *J. Chem. Soc. Abs.*, 72 (I), 522 (1897).

m.p. 102°. When double the above quantities of aluminum chloride and chloroacetyl chloride are used, bis(chloroacetyl)anisole, $H_3COC_6H_3(COCH_2Cl)_2$ (m.p. 106°), is obtained.

In reacting chloroacetyl chloride with anisole, Tutin[511] reported the formation also of the *o*-isomer. One molecular proportion of anisole was mixed with more than the equivalent quantity of the acetyl chloride and then diluted with carbon disulfide. A molecular proportion of aluminum chloride was carefully added, under cooling. After three hours the solvent was decanted, the reaction was treated with water and HCl and then extracted with ether. The ethereal liquid was shaken with sodium hydroxide in order to remove impurities, and the solvent was then evaporated. Upon fractional crystallization from alcohol there was obtained, for the most part, *p*-(chloroacetyl)anisole (m.p. 102°) and the *o*-isomer, m.p. 69°. This work was later repeated and confirmed by Auwers and Leo.[512] From bromoacetyl bromide and anisole, *p*-(bromoacetyl)anisole has been prepared.[513]

The reaction of propionyl chloride and anisole has been studied by Gattermann,[505] who reports that the chief reaction product was *p*-propionylanisole (m.p. 27°, and b.p. 273-275°) but that some dianisylpropylene, $(C_6H_4OCH_3)_2C{:}CHCH_3$, is also formed. Klages[514] states that the formation of large amounts of the propylene compound are avoided by working at a temperature of −5° and using petroleum ether instead of carbon disulfide as solvent. Using 60 g of anisole and 80 g of propionyl chloride, he obtained a yield of 55 g of propionyl anisole, b_{14} 148°. Using carbon disulfide as solvent, however, Baranger[509] reported a 93 per cent yield of propionylanisole, b_{19} 149-150.5° and m.p. 20.5°.

By the action of aluminum chloride on a solution of anisole and butyryl chloride in light petroleum, Skraup and Nieten[515] secured a 46.5 per cent of theoretical yield of *p*-butyrylanisole, b.p. 162-163°/20 mm. and m.p. −3° to −4°. They state that, if light petroleum is replaced by carbon disulfide, the yield of the ketone is decreased to only 29.2 per cent because the product is contaminated with α,α-di-*p*-anisyl-α-butylene, $(CH_3O.C_6H_4)_2C{:}CH.C_2H_5$. This is the same type of olefin substitution as was secured by Gattermann[516] in his reaction of anisole with acyl chlorides using carbon disulfide as solvent.

Baranger[509] secured a 91 per cent yield of *p*-butyrylanisole (b_{19} 158-159°, m.p. 21-22°) by reacting anisole with butyryl chloride in anhydrous carbon disulfide in the presence of aluminum chloride.

Using the process of Klages,[514] in which petroleum ether was used as solvent and the reaction temperature was held at about −5°, Skraup

[511] F. Tutin, *J. Chem. Soc.*, **97**, 2503 (1910)
[512] K. v. Auwers and M. Leo, *Ber.*, **59**, 2899 (1926).
[513] F. Kunckell and W. Scheven, *Ber.*, **31**, 172-174 (1898).
[514] A. Klages, *Ber.*, **35**, 2262-2267 (1902).
[515] S. Skraup and F. Nieten, *Ber.*, **57**, 1294-1310 (1924); *J. Chem. Soc. Abs.*, **126** (I), 1185 (1924).
[516] L. Gattermann, R. Ehrhardt, and H. Maisch, *Ber.*, **22**, 1129-1133 (1889); *J. Chem. Soc. Abs.*, **56**, 862 (1889); *Ber.*, **23**, 1199-1210 (1890); *J. Chem. Soc. Abs.*, **58**, 963 (1890).

and Nieten [515] reacted anisole with the indicated acid chlorides and obtained the following ketones:

Acid Chloride Used	Ketone Obtained	b.p.	m.p.	% yield
n-Valeroyl chloride	*p*-valeroylanisole	165-7°/14 mm.	26°	42.9
n-Caproyl chloride	*p*-caproylanisole		41°	52.1
Heptanoyl chloride	*p*-heptanoylanisole	192°/17 mm.	40°	43.3
Nonanoyl chloride	*p*-nonanoylanisole		43°	38.2

The production of a 99 per cent yield of *p*-heptanoylanisole (b_{25} 203°, m.p. 43°) was reported by Baranger.[509] He used anhydrous carbon disulfide as solvent in the presence of aluminum chloride. The reaction of anisole with palmitoyl chloride has also been reported.[517]

The reaction of oxalyl chloride with anisole and aluminum chloride in carbon disulfide solution gives anisil (m.p. 132°) in 90 per cent yield,[518] according to the scheme:

$$2CH_3O.C_6H_5 + COCl\ COCl \xrightarrow{AlCl_3} CH_3O\ C_6H_4\ CO\ CO.C_6H_4.OCH_3$$

Although oxalyl chloride fails to give diketones with less reactive compounds, due to decomposition of the acid halide by the aluminum chloride before Friedel-Crafts condensation, the reaction proceeds normally with a number of phenol ethers.

The chloride of ethyl chloroglyoxylate also reacts normally with phenol ethers,[519] the condensation occurring:

$$RO.C_6H_5 + ClCO\ COOC_2H_5 \qquad RO.C_6H_4\ CO.COOC_2H_5 + HCl$$

Glutaryl chloride, $COCl.CH_2\ CH_2.CH_2.COCl$, condenses with anisole to give α,γ-dianisoylpropane (m.p. 99°), and in its asymmetrical form reacts to give α,α-di-*p*-anisylvalerolactone, m.p. 111-113°.[520]

Fumaryl chloride with anisole gives only a small yield of dianisoylethylene, the reaction between anisole and fumaryl chloride being unexpectedly difficult.[521] The condensation proceeded normally, however according to the equation:

$$ClCOCH : CHCOCl + 2CH_3O.C_6H_5 \xrightarrow{AlCl_3}$$

$$CH_3O.C_6H_4.CO.CH : CHCO.C_6H_4.OCH_3 + 2HCl$$

The reaction of benzoyl chloride with anisole was reported by Gattermann and co-workers [516] who described the production of *p*-benzoylanisole, m.p. 61-62°.

Peterson [522] obtained *p*-chloro-*p'*-methoxybenzophenone, $C_6H_4Cl.CO.C_6H_4.OCH_3$ (m.p. 125°) by the action of anisole on *p*-chlorobenzoyl chloride in the presence of aluminum chloride. He similarly prepared

[515] P. Krafft, *Ber.*, 21, 2265-2271 (1888).
[516] H. Staudinger, *Ber.*, 45, 1594-1598 (1912); P. C. Mitter and H. Mukherjee, *J. Ind. Chem. Soc.* 16, 266-5 (1939); *C. A.*, 34, 2258.
[517] L. Bouveault, *Bull. soc. chim. (3)*, 15, 1014-1021 (1897).
[518] G. P. Plant and M. E. Tomlinson, *J. Chem. Soc.*, 1935, 856; *C. A.*, 29, 5817.
[519] J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, 45, 1303-1307 (1923).
[520] P. P. Peterson, *Am. Chem. J.*, 46, 325-344 (1911); *J. Chem. Soc. Abs.*, 1911 (I), 870.

o-chloro-*p'*-methoxybenzophenone (b.p. 250°/50 mm), using *o*-chlorobenzoyl chloride. Bergmann and Bondi [523] reported that the m.p. of the *p*-compound prepared by them from *p*-chlorobenzoyl chloride and anisole in the presence of carbon disulfide and aluminum chloride was 127°.

Anisole and *o*-bromobenzoyl chloride have been condensed in the presence of anhydrous aluminum chloride to give methoxy-*o'*-bromobenzophenone, m.p. 95-95.5°.[524]

Phenoxyacetyl chloride has been reacted with anisole to give *p*-anisyl phenoxymethyl ketone, melting at 67°.[525]

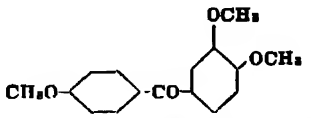
Cinnamoyl chloride was condensed with anisole by Bergmann and Wolff [526]; 44 g of anisole and 67 g of cinnamoyl chloride were used with 100 cc of carbon disulfide and 50 g of aluminum chloride. The reaction was a vigorous one and was completed by four hours of boiling on a water-bath. The mass was decomposed by means of ice and fuming HCl, the solution dried and distilled. The unsaturated ketone which was obtained, benzal-*p*-methoxyacetophenone, boils at 265° and melts at 107°. The ketone had previously been prepared in the same way by Stockhausen and Gattermann.[527]

The latter also reacted anisole with an acid chloride containing a triple bond, phenylpropiolic acid chloride, $C_6H_5C{:}C.COCl$, and obtained a ketone, $C_6H_5C{:}COC_6H_4OCH_3$, m.p. 100°. Evidently the presence of unsaturated bonds does not interfere with expected ketone formation.

By the interaction of anisole with diphenic acid chloride and aluminum chloride, 2,2'-dianisoylbiphenyl (m.p. 115°) has been prepared.[528]

Anisyl chloride reacts easily with anisole in the presence of aluminum chloride in carbon disulfide to give *p,p'*-dimethoxybenzophenone, $C_6H_4(OCH_3).CO.C_6H_4.OCH_3$, m.p. 144°.[529]

Mauthner [530] reported the condensation of 3,5-dimethoxybenzoyl chloride with anisole in carbon disulfide solution in the presence of aluminum chloride with the formation of 3,5,4'-trimethoxybenzophenone, m.p. 97-98°. Veratroyl chloride was condensed with anisole by Kostanecki and Tambor [531] to give 3,4,4'-trimethoxybenzophene, m.p. 98-99°. It has the following structure:



[523] E. Bergmann and A. Bondi, *Ber.*, **64**, 1471 (1931); *Brit. Chem. Abs.*-A, 1931, 947.
[524] A. Heidenreich, *Ber.*, **27**, 1452-1456 (1894).
[525] R. Stoermer and P. Atenstädt, *Ber.*, **35**, 3560-3565 (1902).
[526] E. Bergmann and H. A. Wolff, *J. Am. Chem. Soc.*, **54**, 1644-1647 (1932).
[527] F. Stockhausen and L. Gattermann, *Ber.*, **25**, 3535-3538 (1892); *J. Chem. Soc. Abs.*, **64** (I) 163 (1893).
[528] Frank Bell and Fred Briggs, *J. Chem. Soc.*, 1936, 1561-1568.
[529] H. Schnaekenberg and R. Scholl, *Ber.*, **36**, 654-655 (1903). H. Staudinger and N. Kon, *Ann.*, **384**, 101 (1911).
[530] F. Mauthner, *J. prakt. Chem.*, **87** (II), 403-409 (1913); *J. Chem. Soc. Abs.*, **104** (I), 633 (1913); *C. A.*, **7**, 3544.
[531] St. v. Kostanecki and J. Tambor, *Ber.*, **39**, 4032-4037 (1906).

Coumarilyl chloride has been similarly reacted with anisole to give 4-methoxy-1-benzoylcoumarone.[532]

2,3-Hydroxynaphthoyl chloride is claimed to react with anisole in the presence of aluminum chloride to yield *p*-anisyl 3-hydroxy-2-naphthyl ketone, m.p. 134-134.5°. Similarly the reaction of *m*-4-xylenol-5-carboxylyl chloride with anisole is claimed to give 2-hydroxy-4'-methoxy-3,5-dimethylbenzophenone (*p*-anisyl 4-hydroxy-*m*-5-xylyl ketone) m.p. 105-106°.[533]

The condensation of fluorenone-4-carboxylyl chloride with anisole in the presence of aluminum chloride leads to the formation of 4-*p*-methoxybenzoyl)fluorenone, m.p. 95°.[534]

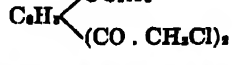
Phenetole and Higher Alkyl Ethers of Phenol

Phenetole has been condensed with numerous acid chlorides, the reaction proceeding with easy formation of the corresponding ketone. Gattermann and co-workers[535] reacted phenetole with acetyl chloride in the presence of aluminum chloride and carbon disulfide and obtained *p*-acetylphenetole, m.p. 60-61°. With propionyl chloride they secured *p*-propionylphenetole, m.p. 30°. Böeseken[536] secured a 96 per cent of theoretical yield of the acetyl compound by the gradual addition of a mixture of 50 g of acetyl chloride and 50 g of phenetole to 100 g of aluminum chloride covered with a layer of boiling carbon disulfide. He attributed the high yield to the presence of an excess of aluminum chloride.

Klages[537] used petroleum ether as the solvent and kept the temperature at less than 5°. He secured 23 g of propionylphenetole from 25 g of phenetole. Klages also used petroleum ether as solvent in the preparation of butyrylphenetole (b.p. 173-174°) from phenetole and butyryl chloride. From isobutyryl chloride and phenetole with aluminum chloride and carbon disulfide, Gattermann and co-workers[538] reported the preparation of isobutyrylphenetole, m.p. 41°.

Using Klages' method for the preparation of *p*-propionylphenetole, Johnson and Hodge[539] reported that they secured excellent yields.

Chloroacetyl chloride was reacted with phenetole by Kunckell and Johannssen.[540] They used 15 g of phenetole, 20 g of chloroacetyl chloride, and 45 g of aluminum chloride with carbon disulfide as diluent. The product obtained was a diketone, a bis-(chloroacetyl)phenetole,



[532] F. Zwayer and S. Kostanecki, *Ber.*, 41, 1335-1341 (1908).
[533] Brit. P. 305,769 (1927); French P. 646,402 (1928) to I. G.; *Brit. Chem. Abs.*-B, 276 (1929)
[534] Hans Pick, *Monatsh.*, 25, 979-986 (1904); *J. Chem. Soc. Abs.*, 88 (I), 68 (1905).
[535] L. Gattermann, R. Ehrhardt, and H. Maisch, *Ber.*, 22, 1129-1133 (1889); *J. Chem. Soc* (London), 56, 862 (1889); *Ber.*, 23, 1199-1210 (1890); *J. Chem. Soc. Abs.*, 58, 963 (1890)
[536] J. Böeseken, *Bull. soc. chim.*, 19, *(3)*, 349-350 (1898); *J. Chem. Soc. Abs.*, 76 (I), 435 (1899)
[537] A. Klages, *Ber.*, 35, 2262-2267 (1902).
[538] L. Gattermann, R. Ehrhardt, and H. Maisch, *Ber.*, 23, 1199-1210 (1890).
[539] T. B. Johnson and W. W. Hodge, *J. Am. Chem. Soc.*, 35, 1014-1023 (1913).

The formation of a diketone here may perhaps be explained by the slight excess of the chloride used as well as the large amount of catalyst.

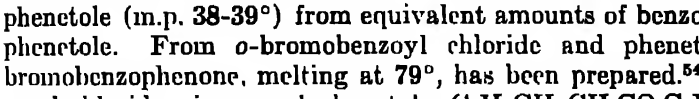
With dichloroacetyl chloride the same workers obtained the monoketone, dichloroacetylphenetole, m.p. 73°.[540] Using bromoacetyl chloride, Kunckell and Scheven[541] obtained *p*-(bromoacetyl)phenetole (m.p. 59-60°) or the diketone, a bis(bromoacetyl)phenetole (m.p. 77°) depending on the amount of the chloride used.

Phenetole and oxalyl chloride yield 4,4'-diethoxybenzil in the presence of aluminum chloride.[542] The reaction takes place readily, the yield of the diketone being almost quantitative.

With the chloride of glutaric acid, $COCl.CH_2.CH_2.CH_2COCl$, and phenetole Plant and Tomlinson[543] obtained disubstitution. They used aluminum chloride in carbon disulfide and obtained 1,3-diphenetoylpropane, m.p. 133°.

Gattermann and co-workers[544] report the preparation of benzoylphenetole (m.p. 38-39°) from equivalent amounts of benzoyl chloride and phenetole. From *o*-bromobenzoyl chloride and phenetole, ethoxy-*o'*-bromobenzophenone, melting at 79°, has been prepared.[545] With cinnamoyl chloride, cinnamoyl phenetole, $C_6H_5CH{:}CH.CO.C_6H_4OC_2H_5$ (m.p. 74-75°) is obtained.[546]

Phenetole has been condensed with phenoxyacetyl chloride with the production of phenetyl phenoxymethyl ketone (m.p. 102°) according to the reaction[547]:



Phthaloyl chloride and phenetole react in the presence of aluminum chloride to give diphenetyl phthalide.[548]

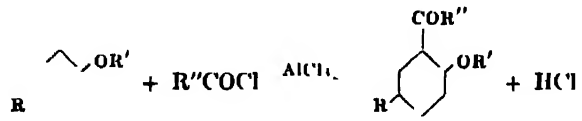
The reaction of phenyl propyl ether with benzoyl chloride to give *p*-propoxybenzophenone (m.p. 65-66°) has been reported.[549] Phenyl isobutyl ether and propionyl chloride have been reacted. 100 g of aluminum chloride was cooled and to it was added a solution of 70 g of propionyl chloride in 150 g of petroleum ether. This was then slowly treated with phenyl isobutyl ether. The product, 1-propionyl-4-isobutoxybenzene, melted at 52°, and boiled at 172-174°/14 mm.[550]

[540] F. Kunckell and F. Johannsen, *Ber.*, 31, 172 (1898).
[541] F. Kunckell and W. Scheven, *Ber.*, 31, 172-174 (1898).
[542] A. Schönberg and O. Kraemer, *Ber.*, 55, 1174-1194 (1922); *J. Chem. Soc. Abs.*, 122 (I), 663 (1922).
[543] S. G. P. Plant and M. E. Tomlinson, *J. Chem. Soc.*, 1935, 856; *C. A.*, 29, 5817.
[544] L. Gattermann, R. Ehrhardt, and H. Maisch, *Ber.*, 22, 1129-1133 (1889); *J. Chem. Soc. Abs.*, 56, 862 (1889); *Ber.*, 23, 1199-1210 (1890); *J. Chem. Soc. Abs.*, 58, 963 (1890).
[545] A. Heidenreich, *Ber.*, 27, 1452-1456 (1894).
[546] F. Stockhausen and L. Gattermann, *Ber.*, 25, 3535-3538 (1892); *J. Chem. Soc. Abs.*, 64 (I), 165 (1893).
[547] R. Stoermer and P. Atenstadt, *Ber.*, 35, 3560-3565 (1902).
[548] A. Haller and A. Guyot, *Compt. rend.*, 120, 296-299 (1895); *J. Chem. Soc. Abs.*, 68 (I), 370 (1895).
[549] C. Torres and Gonsales, *Bull. soc. chim. (4)*, 37, 1591-1596 (1925).
[550] A. Klages, *Ber.*, 35, 2262-2267 (1902).

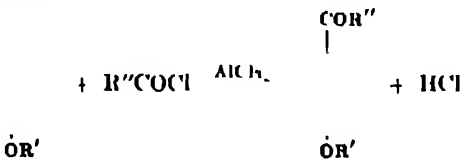
Ethers of Alkyl Phenols and Acyl Chlorides

Variously substituted ethers have been reacted with acyl chlorides in the presence of anhydrous aluminum chloride. Whereas with unsubstituted ethers the entering acyl group generally goes *para-* to the ether linkage, the orientation of the entering group in the acylation of substituted ethers is influenced by the nature of the alkyl substituent.

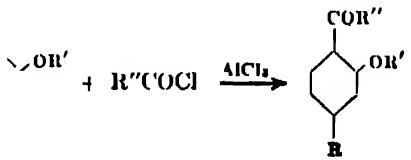
Thus in the reaction of *p*-alkyl-substituted ethers with acyl chloride, the entering group goes *o-* to the ether linkage:



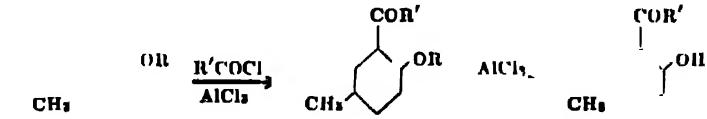
With *o*-alkyl-substituted ethers and acyl chloride the entering group goes *p-* to the ether linkage:



With *meta*-alkyl substituted ethers substitution is *ortho-* to the ether linkage:



Betteridge [551] reacted various acid chlorides with the methyl and ethyl ethers of *p*-cresol in carbon disulfide solution in order to obtain the corresponding acylated ethers. Upon further treatment of these ketonic ethers with aluminum chloride, according to the method of Hartmann and Gattermann,[552] he secured the phenolic ketones:



In this way Betteridge prepared what he reported to be *o*-acetyl-*p*-cresol (m.p. 50°) and *o*-propionyl-*p*-cresol, m.p. 2°.

Hill and Graf [553] found that when petroleum ether, instead of carbon

[551] F. H. Betteridge, Diss., Breslau (1906).
[552] C. Hartmann and L. Gattermann, *Ber.*, **25**, 3531-3534 (1892); *J. Chem. Soc. Abs.*, 1893 (I), 152
[553] A. J. Hill and L. E. Graf, *J. Am. Chem. Soc.*, **37**, 1839-1846 (1915), *J. Chem. Soc. Abs.*, 108 (I), 980 (1915)

disulfide, was used as the diluting medium in the Friedel-Crafts reaction, the demethylation or de-ethylation took place during the reaction. They slowly added 25 cc of acetyl chloride to a solution of 30 g of the methyl ether of *p*-cresol in 200 cc of dry petroleum ether, using 25 g of aluminum chloride. The mixture was heated for thirty hours on a steam-bath. After removal of solvent, decomposition of complex catalyst, and extraction with ether, 16 g of the hydroxy ketone were yielded by the fraction b. 237-247°. The melting point of the product was 49° and it was proved to be 2-hydroxy-5-methylacetophenone. The melting point given by Betteridge for his *o*-acetyl-*p*-cresol was 50°. Auwers also prepared *o*-acetyl-*p*-cresol (m.p. 50°) from *p*-cresol methyl ether and acetyl chloride.[554] In a similar way, using propionyl chloride, Hill and Graf prepared 2-hydroxy-5-methylpropiophenone, b_{40} 153°, m.p. 2°. The physical properties of this compound were found to agree with the *o*-propionyl-*p*-cresol prepared by Betteridge. The compound had also been prepared, according to the method of Betteridge, by von Auwers,[555] who reported the b.p. to be 123°/11 mm and 129-130°/16.5 mm. von Auwers [556] also reports the preparation of 3-methyl-6-hydroxypropiophenone, b.p. 135-140°/22 mm, m.p. −2°.

Using Betteridge's method, von Auwers [556] also prepared the following hydroxy- ketones from *p*-tolyl ethyl ether and the corresponding acid chlorides:

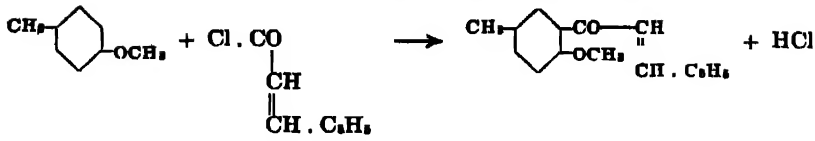
3-methyl-6-hydroxy-*n*-butyrophenone, $CH_3.OH.C_6H_3.CO.C_3H_7$, m.p. 37°. Its ethyl ether has a b.p. of 205°/10 mm.
3-methyl-6-hydroxybenzophenone, $CH_3.OH.C_6H_3.CO.C_6H_5$, m.p. 84°. Its ethyl ether melts at 68°.

Reacting 1 mole of *p*-cresol methyl ether with 3 moles of acetyl chloride, von Auwers [557] secured *o,o*-diacetyl-p-cresol, m.p. 82-83°. Using chloroacetyl chloride instead of acetyl chloride with twice the molecular proportion of aluminum chloride, he secured *o*-(chloroacetyl)-*p*-cresol, m.p. 63°.

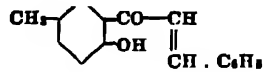
Condensation of anisoyl chloride with *p*-cresol methyl ether and aluminum chloride in carbon disulfide gives 2,4'-dimethoxy-5-methylbenzophenone (m.p. 69-70°) together with its methoxy- cleavage product, 2-hydroxy-4'-methoxy-5-methylbenzophenone. Here again is illustrated the easy saponification of the methoxy- group *ortho*- to the carbonyl.[558]

By means of the Friedel-Crafts reaction, phenol ethers whose *p*-position is protected by a substituent can be condensed to chalcone ethers by using cinnamoyl chloride. Thus, Simonis and Lear [559] secured, with *p*-tolyl methyl ether and cinnamoyl chloride, the compound 5-methyl-2-methoxychalcone, m.p. 55-56°.

[554] K. v. Auwers, M. Lechner, and H. Bundesmann, *Ber.*, **58**, 36-51 (1925).
[555] K. von Auwers, *Ber.*, **47**, 2819 (1914); *Ber.*, **58**, 36-51 (1925).
[556] K. v. Auwers, *Ber.*, **36**, 3890-3892 (1903); *J. Chem. Soc. Abs.*, **86** (I), 66 (1904).
[557] K. von Auwers, *Ann.*, **364**, 164-167 (1909).
[558] K. v. Auwers and E. Reits, *Ber.*, **40**, 3514-3521 (1907).
[559] H. Simonis and C. Lear, *Ber.*, **39**, 2905-2913 (1936); *C. A.*, **21**, 1255.

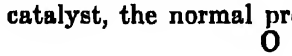


The foregoing reaction takes place if only 1 mole of aluminum chloride in carbon disulfide is used with molecular proportions of the ether and the chloride. If, however, 2 moles of aluminum chloride are used, demethylation of the methoxy- group occurs and the hydroxychalcone,



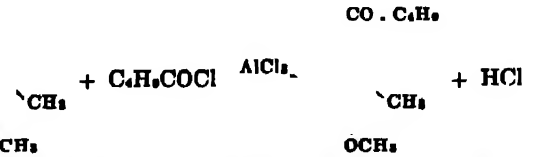
(m.p. 111°) is secured in 40 per cent yield. The same product can also be secured by heating with aluminum chloride the methoxychalcone secured by using only 1 mole of the catalyst. Here the methoxy- group splits off, according to Hartmann and Gattermann.[552] The success of the reaction involving the one-step production of the hydroxychalcone depends on adding the aluminum chloride very slowly to the ether and chloride in carbon disulfide and slowly raising the temperature until the reaction has reached an end at about 50°.

An acid chloride containing a triple bond, phenylpropiolic acid chloride, was also condensed with *p*-cresol methyl ether by Simonis and Lear.[559] Under strong cooling and using molecular proportions of the reactants and catalyst, the normal product, 5-methyl-2-methoxyphenyl-



propiolophenone, $CH_3(CH_3O)C_6H_3.\overset{\overset{O}{\|}}{C}.C{:}C.C_6H_5$ (m.p. 62°) was obtained. However, when two molecular proportions of aluminum chloride were used, and the reaction temperature was allowed to climb from −4° to room temperature, an unexpected product, 5-methyl-2-hydroxy-β-chlorochalcone, $(CH_3)(OH).C_6H_3.CO.CH{:}CCl.C_6H_5$ (m.p. 95.5° was obtained in 60 per cent yield. Here the excess of aluminum chloride had caused addition of hydrogen chloride to the triple bond as well as hydrolysis of the methoxy- group.

o-Cresol methyl ether has been condensed with acyl halides of more than four carbon atoms for the preparation of higher alkylated *o*-cresols by reduction of the primarily formed ketones.[560] The preparation of 4-methoxy-3-methyl-*n*-valorophenone (b.p. 151-155°/5 mm) has been described.



[560] U. S. P. 1,930,923 (1933) to W. G. Christiansen and W. S. Jones (to E. R. Squibb & Sons), *Brit. Chem. Abs.*-B, 874 (1934).

Clemmensen reduction and demethylation of the phenone is said to result in the formation of 5-*n*-amyl-*o*-cresol.

Koenigs and Carl [561] gradually treated a mixture of 5 g of *o*-cresol methyl ether and 5.5 g of benzoyl chloride in 25 cc of carbon disulfide with 10 g of aluminum chloride and secured a 75 per cent yield of the methyl ether of *o*-cresyl phenyl ketone,

$$C_6H_5CO \cdot C_6H_3\begin{cases}CH_3 & (1)\\ OCH_3 & (2)\end{cases}, \text{ melting at } 80°.$$

m-Cresol methyl ether has been reacted with phthaloyl chloride by Weiss and Knapp [562] in the presence of aluminum chloride and carbon disulfide. Condensation occurred *ortho-* to the methoxyl group, giving 3′,3″-dimethoxydi-*p*-tolylphthalide. Using *m*-methoxybenzoic acid or its methyl ester instead of *m*-cresol methyl ether, they obtained 4′-methoxybenzophenone-2,2′-dicarboxylic acid dilactone, m.p. 183°.

When von Auwers [563] gently heated an equimolecular mixture of the methyl ether of *sym-meta*-xylenol with acetyl chloride diluted with carbon disulfide and treated it with aluminum chloride, he obtained the methyl ether of *o*-acetyl-*sym-m*-xylenol, b.p. 135°/14 mm and m.p. 48-49°. However, using larger amounts of aluminum chloride, and heating the reaction mixture for an hour on a water-bath, he secured *o*-acetyl-*sym-m*-xylenol, b.p. 140-141°/18 mm and m.p. 57-58°. In both cases the carbonyl group is attached at the *ortho-* position to the hydroxyl of the original phenol. If the hydroxyl group of the xylenol is acetylated before the Friedel-Crafts reaction, the ketonic group attaches itself again in the same position, the *para-* isomeride being absent from the product. The exclusive formation of the *o*-isomeride is still more remarkable in the fact that if a second acetyl radical attaches itself to the ring during the Friedel-Crafts condensation, it enters at the remaining *ortho-* position. Thus, *o,o*-diacetyl-*sym-m*-xylenol (m.p. 109-110°) is obtained.

The orienting influence of the *meta-* methyl groups is stronger than that of the methoxy- group. Thus when 2,4-xylenol methyl ether and benzoyl chloride in carbon disulfide are gradually added to aluminum chloride also in carbon disulfide, there is obtained a 60 per cent yield of 3-methoxy-4,6-dimethylbenzophenone (b.p. 199-200°/12-13 mm) and about an 8 per cent yield of the 3-hydroxy- derivative, m.p. 140-141°.[564]

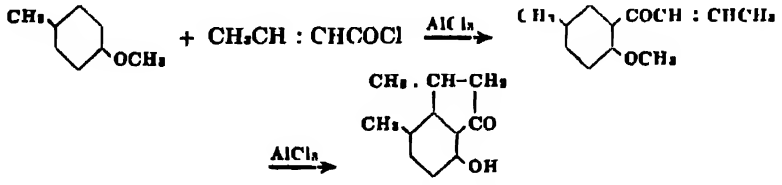
Realizing that this preparation of the *meta-* derivative might make possible the easy preparation of certain *m*-hydroxy- ketones which are otherwise difficult to secure, von Auwers and Mauss [565] wished to see if other phenol ethers of a definite structure would react in the same way. Using acetyl chloride instead of benzoyl chloride, they repeated the above

[561] W. Koenigs and R. W. Carl, *Ber.*, 24, 3889-3900 (1891).
[562] R. Weiss and W. Knapp, *Monatsh.*, 50, 10-15 (1928); *Brit. Chem. Abs.*-A, 1928, 1007; *C. A.*, 22, 3651.
[563] K. v. Auwers, *Ber.*, 48, 90-93 (1915); *J. Chem. Soc. Abs.*, 108 (I), 145 (1915).
[564] J. Meisenheimer, R. Hanssen, and A. Wächterowitz, *J. prakt. Chem.*, 119, 315-367 (1928); *C. A.*, 22, 3887. J. Meisenheimer and R. Hanssen, Dissertation, Tübingen, 1926.
[565] K. v. Auwers and W. Mauss, *Ber.*, 61, 1495-1507 (1928).

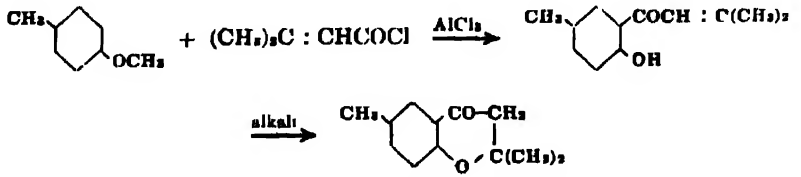
work and obtained 6-acetyl-2,4-xylenol as the chief product, an isomer of this compound, and a methyl ether of the isomer. They showed that the isomer was 5-acetyl-2,4-xylenol and that its ether could easily be hydrolyzed to the phenol. The *m*-hydroxy- ketone was therefore produced also in this case. The same results were obtained using chloroacetyl chloride instead of acetyl chloride, and 2-ethyl-4-methylphenol instead of 2,4-xylenol. With mesityl methyl ether they obtained *m*-acetylmesitol, m p. 81-82°. The symmetrically tri-substituted phenols, therefore, constitute another group of phenols which can give *meta*-derivatives.

The results obtained by von Auwers and Mauss show that alkyls tend to direct an entering acyl group more to the *p*- than the *o*-position to themselves. However, it is seen that the Friedel-Crafts reaction with poly-alkylated phenol ethers may proceed in quite different ways; the structure of the resulting products must be determined in each case.

In another study, von Auwers [506] reacted alkylated phenol ethers with higher acyl halides in order to investigate conditions necessary for effecting ring closure. By the action of crotonyl chloride on *p*-cresol methyl ether, the methyl ether of *o*-propenyl *p*-cresyl ketone was formed. Under the influence of additional aluminum chloride, a rearrangement took place with formation of 3,4-dimethyl-7-hydroxyhydrindone:

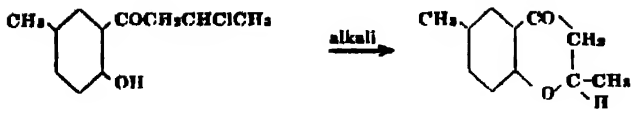


From *p*-cresol methyl ether and β,β-dimethylacrylyl chloride and aluminum chloride *o*-isobutenyl *p*-cresyl ketone was prepared. This was converted to 2,2,6-trimethylchromanone by heating with alkali:

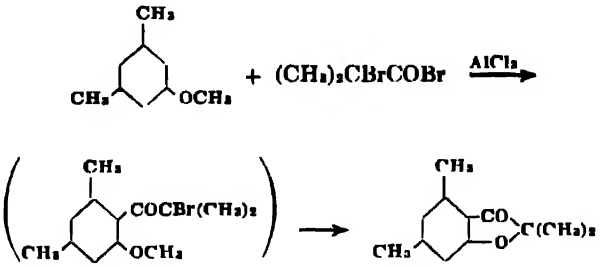


β-Chlorobutyryl chloride with *p*-cresol methyl ether and aluminum chloride similarly gives *o*-(β-chlorobutyryl)-*p*-cresol, which with alkali yields 2,6-dimethylchromanone.

[506] K. v. Auwers, *Ann.*, 421, 1-119 (1920); *C. Z.*, 1920, III, 634-636.

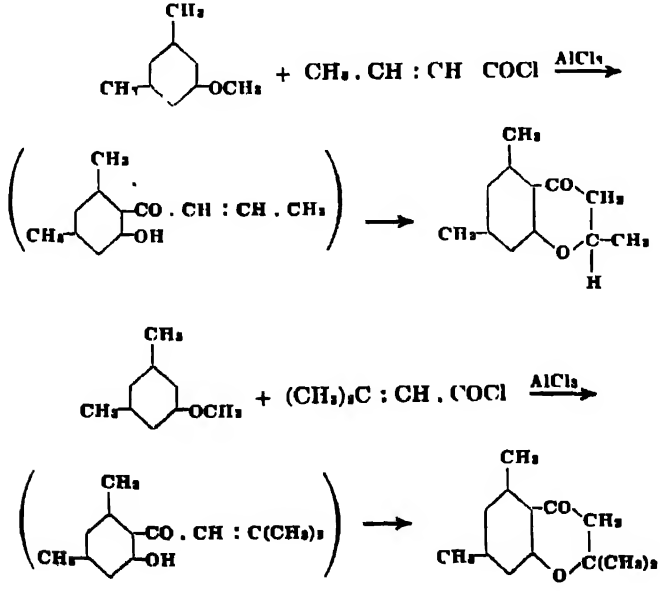


With α-bromoisobutyryl bromide and *sym-m*-xylenol methyl ether, ring closure is effected during the Friedel-Crafts reaction:



Bromine in the ring does not influence the course of the reaction, for *p*-bromo-*sym-m*-xylenol methyl ether with α-bromoisobutyryl bromide under like conditions gives 1,1,3,5-tetramethyl-4-bromocoumaranone.

In the condensation of *sym-m*-xylenol methyl ether with crotonyl chloride in the presence of aluminum chloride, the unsaturated crotonyl xylenol is not formed. Instead, ring closure occurs, with production of 2,5,7-trimethylchromanone (b.p. 164-170°/21 mm), the methoxy- group undergoing cleavage during the reaction:

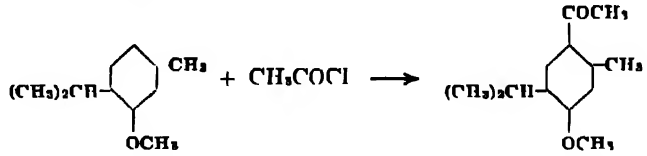


In the same way, 2,2,5,7-tetramethyl chromanone is formed from β,β-dimethylacrylic acid chloride and *sym*-*m*-xylenol methyl ether (see page 313).

Reaction of *sym*-*m*-xylenol methyl ether with isobutyryl chloride, on the other hand, results only in the formation of hydroxy- ketones *p*-Bromoxylenol methyl ether and butyryl chloride yield a ketone also

Similar condensations of *asym*-*o*-xylenol have been studied by von Auwers and Risse.[567]

By careful addition of aluminum chloride to thymol methyl ether in cold acetyl chloride, Kuroda and Nakamura[568] secured 4-methoxy-2-methyl-5-isopropyl acetophenone (b.p. 236°, 157-158°/18 mm) in a theoretical yield, according to the following equation:



Here *p*-substitution to the methoxy- group is secured Verley[569] performed the same reaction at 0° and in a vacuum and also secured an almost theoretical yield of acetothymyl methyl ether, b.p. 155°/22 mm

In a study of the action of oxalyl chloride with phenol ethers it was found[570] that whereas *o*-tolyl methyl ether yields a diketone through Friedel-Crafts replacement of both chlorines, *m*- and *p*-tolyl methyl ethers yield only the corresponding acids, being converted into 3- and 5-methylsalicylic acids, respectively.

Halogenated Phenol Ethers and Acyl Chlorides

The influence of a chloro-substituent on the reaction of anisole with aroyl chlorides has been studied.[571] With aluminum chloride as catalyst and *sym*-tetrachloroethane as solvent at temperatures of 120-130°, the following results are obtained with the indicated monochloro- derivatives of anisole:

Ether	Acid Chloride	Product Obtained	m.p.	Yield
o-	benzoyl	3-chloro-4-hydroxybenzophenone	180-181°	48.3
		3-chloro-4-methoxybenzophenone	99-99.5°	42
p-	benzoyl	5-chloro-2-hydroxybenzophenone	95-95.5°	60.5
		p-chlorophenyl benzoate		22
o-	*o*-toluyl	3-chloro-4-hydroxyphenyl *o*-tolyl ketone	128-129°	25
		3-chloro-4-methoxyphenyl *o*-tolyl ketone	106-106.5°	58
p-	*o*-toluyl	5-chloro-2-hydroxyphenyl *o*-tolyl ketone	67.5-68°	49.7
o-	*m*-toluyl	3-chloro-4-hydroxyphenyl *m*-tolyl ketone	145-146°	14.7
		3-chloro-4-methoxyphenyl *m*-tolyl ketone	105-105.5°	81
	m-toluyl	5-chloro-2-hydroxyphenyl *m*-tolyl ketone	106-106.5°	63

[567] K. v Auwers and E Risse, *Ber.*, **64**, 2216-2222 (1931); *cf* H Simonis and C Lear *Ber.*, **59**, 2908-2913 (1926) H Simonis and S. Danischewski, *Ber.*, **59**, 2914-2919 (1926)
[568] C Kuroda and T. Nakamura, *Sci. Papers Inst. Phys Chem Res Tokyo* **18**, 61-76 (1932) *Brit Chem Abs.-A*, 358 (1932).
[569] A. Verley, *Bull. soc. chim (3)*, **19**, 137-40 (1898); *J Chem. Soc Abs.*, **76** (I), 434
[570] P C Mitter and H. Mukherjee, *J Indian Chem Soc.*, **16**, 393-5 (1939) *C* **4**, **34**, 2358
[571] M. Hayashi, *J pharm. Chem. (II)*, **123**, 289-312 (1929); *Brit Chem Abs.-A*, 89 (1930)

It will be noted that in the case of the reaction of the *p*-chloroanisole with *o*- and *m*-toluyl chloride, as well as with benzoyl chloride, methoxy-cleavage occurred. In no case was the ether halogen affected.

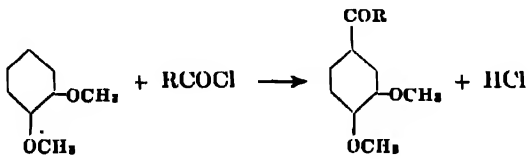
An interesting reaction is that of *p*-chloroanisole with α-bromoisobutyryl bromide and aluminum chloride in carbon disulfide,[572] with formation of 4-chloro-2(α-hydroxyisobutyryl)phenol. Here not only is there demethylation of the alkoxy- group, but also hydrolysis of the α-bromine. The condensation of *o*-bromoanisole with phthaloyl chloride and aluminum chloride leads to the formation of dibromophenolphthalein dimethyl ether.[573]

It has recently been found [574] that aryloxy alkyl ethers of the type $R.O.CH_2CH_2Cl$ and $R.O.CH_2CH_2.O.CH_2CH_2Cl$, where R is any aryl nucleus, condense with acyl halides in the presence of anhydrous aluminum chloride to yield the corresponding acyl derivative without affecting the terminal halogen. Thus by adding a solution of 67 g of β-phenoxy-β′-chlorodiethyl ether and 16.5 g of acetyl chloride to 50 g of aluminum chloride and 200 cc of carbon disulfide, β-acetylphenoxy-β′-chlorodiethyl ether (b.p. 210-225°/10 mm) is obtained. The acetyl chloride can be replaced by other acid chlorides, such as lauroyl chloride, stearoyl chloride, or caproyl chloride.

Ethers of Polyhydroxy Phenols and Acyl Halides

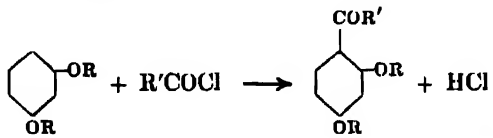
Friedel-Crafts reaction with ethers of polyhydroxy- phenols and acyl halides proceeds smoothly in the presence of aluminum chloride, the only complication being the somewhat easy cleavage of the methoxy- group *ortho-* to the acyl group, under influence of the catalyst.

With *o*-dimethoxy benzene, substitution of the acyl group is *para-meta,* the reaction being:



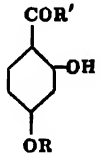
Here, except under prolonged heating or use of excess catalyst, demethylation does not occur.

m-Dialkoxy- benzenes give *ortho-para* substitution products; with resorcinol ethers the reaction is:

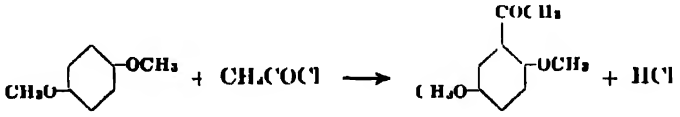


[572] K. v. Auwers, H. Baum, and H. Lorenz, *J. prakt. Chem.*, 115 (2), 81-106 (1927); *Brit. Chem. Abs.*-A, 670 (1927).
[573] E. Grande, *Gazz.*, 27, (2), 67-70 (1897); *J. Chem. Soc. Abs.*, 1897, I, 623.
[574] H. A. Bruson and J. W. Eastes, *J. Am. Chem. Soc.*, 60, 2502-2505 (1938); U. S. P. 2,132,675 (1938) to H. A. Bruson and J. W. Eastes (to Rohm and Haas Co.); British P. 506,301 (1939) to Rohm and Haas Co.

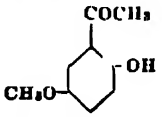
Since here, one of the alkoxy- groups is *ortho-* to the acyl, demethylation may occur during condensation, the product being



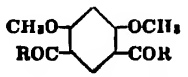
The *para*-methoxy- group strongly resists demethylation; therefore, dihydroxy- ketones are not obtained. Acylation of *p*-dihydroxybenzene ethers results in *ortho-meta* substitution. Thus, hydroquinone dimethyl ether with acetyl chloride gives 2,5-dimethoxyacetophenone:



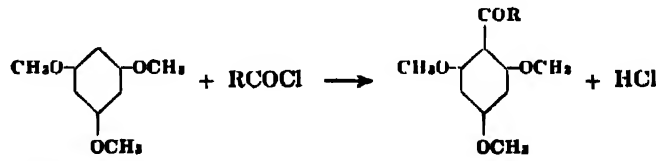
Or, cleavage of *o*-methoxy- may give 2-hydroxy-5-methoxyacetophenone



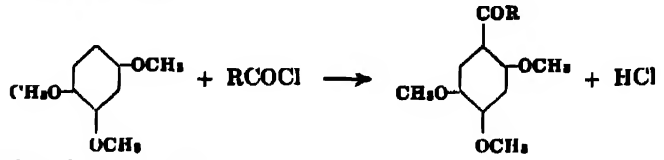
Since the methoxy- group has an activating effect in the Friedel-Crafts reaction, use of two molecular equivalents of acyl halide may result in the production of diketones. With resorcinol ethers, for example, the product may be



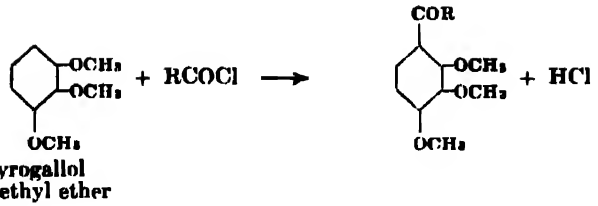
Ethers of trihydroxyphenols are acylated according to the schemes



Phloroglucinol trimethyl ether



Hydroxyhydroquinone trimethyl ether

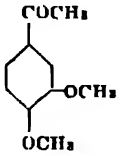


Pyrogallol trimethyl ether

Since the entering acyl group always occupies a position *ortho-* to one of the methoxy- groups, demethylation often results.

Veratrole

The condensation of veratrole with acetyl chloride has been reported by various investigators [575] to proceed with production of 3,4-dimethoxyacetophenone,



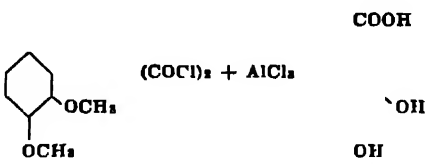
A theoretical yield of the ketone has been obtained by dissolving veratrole in an excess of acetyl chloride, and then gradually adding, with stirring, a molecular equivalent of aluminum chloride.[576]

With chloroacetyl chloride, the expected ω-chloro-3,4-dimethoxyacetophenone is formed,[577] together with a small amount of a demethylated product.[578] It has been found that the type of solvent used regulated the kind of product obtained.[579] With carbon disulfide and with petroleum ether a mixture of the methylated and the free hydroxy- compound was produced. Using nitrobenzene, and heating the reaction mixture for eight hours at 40°, the yield of the hydroxy- compound, ω-chloro-3,4-dihydroxyacetophenone (m.p. 173°) was increased to 82 per cent of the veratrole used. This cleavage of both *meta-* and *para*-methoxy- groups is unusual.

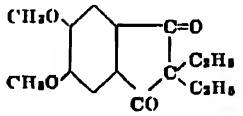
Other condensations of veratrole with aliphatic acyl halides and aluminum chloride which have been reported include those with propionyl chloride,[580] α-bromopropionyl bromide,[581] myristyl chloride, pentadecyl chloride,[582] and palmitoyl chloride.[583] Using petroleum ether as solvent, a practically theoretical yield of myristylveratrole has been secured.[583]

[575] A. Pictet and A. Gams, *Compt. rend.*, 149, 210-212 (1909); *Ber.*, 42, 2943-2952 (1909); *J. Chem. Soc. Abs.*, 96, (I), 871 (1909). C. Mannich, *Archiv der pharmazie*, 248, 137 (1910).
[576] C. Kuroda and T. Matsukuma, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 18, 51-60 (1932); *Brit. Chem. Abs.-A*, 388 (1932).
[577] Bargellini and Forlì-Forti, *Gazz. chim ital.*, 41, I, 754 (1911).
[578] F. Tutin, *J. Chem. Soc.*, 97, 2509 (1910).
[579] H. Stephen and C. Weizman, *J. Chem. Soc.*, 105, 1040 (1914).
[580] T. B. Johnson and W. W. Hodge, *J. Am. Chem. Soc.*, 35, 1014-1023 (1913). Martegiani, *Gazz. chim. ital.*, 42, II, 347 (1913). R. D. Haworth and D. Woodcock *J. Chem. Soc.*, 809-813 (1938).
[581] A. B. Cramer and H. Hibbert, *J. Am. Chem. Soc.*, 61, 2204-2206 (1939).
[582] R. Majima and I. Nakamura, *Ber.*, 46, 4089-4095 (1913); *J. Chem. Soc. Abs.* (I), 167 (1914).
[583] R. Majima and I. Nakamura, *loc. cit.*; T. B. Johnson and Ed. F. Kohmann, *J. Am. Chem. Soc.*, 36, 1259-1268 (1914).

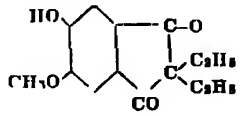
Oxalyl chloride with veratrole has been reported to give 2,3,2',3'-tetramethoxybenzophenone together with a small amount of veratril.[584] The formation of the benzophenone is doubtless due to intermediate decomposition of the acid chloride by aluminum chloride. Veratril is the diketone which would be expected from the reaction. In subsequent work [585] on the reaction, however, the only product was reported to be protocatechuic acid; here, the oxalyl chloride served to introduce a carboxy-group into the ring, under simultaneous cleavage of the alkoxy- groups



The condensation of veratrole with diethylmalonyl chloride in carbon disulfide in the presence of aluminum chloride was studied by Freund and Fleischer [586] who obtained the four indandiones: 5,6-dimethoxy-2,2-diethylindan-1,3-dione, m.p. 149-151°,

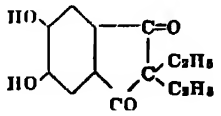


and the corresponding mono- and di-hydroxy- compounds:



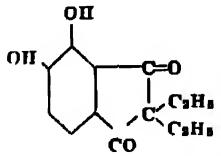
(5-hydroxy-6-methoxy-2,2-diethylindan-1,3-dione, m. p. 106–108°)

and



(5,6-dihydroxy-2,2 diethylindan-1,3-dione, m. p. 216–218°)

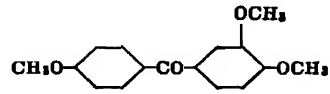
There was also formed the isomer, 4,5-dihydroxy-2,2-diethylindan-1,3-dione, m.p. 116-118°:



[584] H. Staudinger, E. Schlenker, and H. Goldstein, *Helv. chim. acta*, 4, 334-342 (1921); *C. A.* 15, 3445.
[585] P. C. Mitter and H. Mukherjee, *J. Indian Chem. Soc.*, 16, 393-5 (1939); *C. A.*, 34, 2358.
[586] M. Freund and K. Fleischer, *Ann.*, 409, 268-290 (1915).

Benzoyl chloride with veratrole and aluminum chloride yields 3,4-dimethoxybenzophenone.[587] A like reaction takes place with *o*-bromobenzoyl chloride.[588]

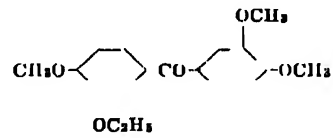
Various methoxy-substituted aroyl chlorides have been condensed with veratrole. Anisole chloride yields 3,4,4′-trimethoxybenzophenone [589]:



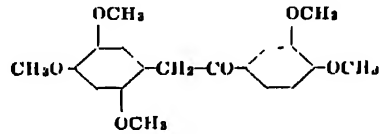
With 3,5-dimethoxybenzoyl chloride, the expected 3,4,3′,5′-tetramethoxybenzophenone (m.p. 114-115°) is obtained.[590]

Veratroyl chloride gives 3,4,3′,4′-tetramethoxybenzophenone, m.p. 144.5-145°.[591]

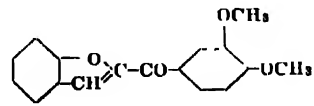
Condensation is also normal with 3-ethoxy-4-methoxybenzoyl chloride, the product being 3,4,4′-trimethoxy-3′-ethoxybenzophenone [592]:



With the chloride of 2,4,6-trimethoxyphenylacetic acid, there is formed also the expected product [593]:



Zwayer and Kostanecki [594] report the preparation of 3′,4′-dimethoxy-2-benzoylcoumarone, .

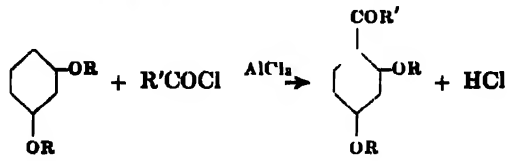


(m.p. 90-91°) from coumarylyl chloride and veratrole in the presence of aluminum chloride.

[587] F. Brüggemann, *J. prakt. Chem. (2)*, 53, 253 (1896); B. König and St. v. Kostanecki, *Ber.*, 39, 4027-4031 (1906).
[588] K. W. Rosenmund and E. Struck, *Ber.*, 52, 1749-1756 (1919).
[589] St. v. Kostanecki and J. Tambor, *Ber.*, 39, 4022-4027 (1906).
[590] F. Mauthner, *J. prakt. Chem. (2)*, 87, 403-409 (1913); *J. Chem. Soc. Abs.*, 104 (1), 632 (1913); *C. A.*, 7, 2544.
[591] St. v. Kostanecki and J. Tambor, *loc. cit.*; B. L. Vanzetti, *Atti. Accad. Lincei, (5)* 24, ii, 467-470 (1915); *J. Chem. Soc. Abs.*, 110, 147 (1916).
[592] T. Omaki, *J. Pharm. Soc. Japan*, 57, 269-274 (1937); *C. A.*, 31, 5347 (1937).
[593] K. Freudenberg and M. Harder, *Ann.*, 451, 210 (1927).
[594] F. Zwayer and v. Kostanecki, *Ber.*, 41, 1335-1341 (1908).

Resorcinol Ethers

Although normal acylation of resorcinol ethers takes the course,

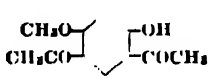


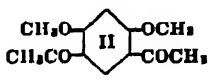
variation of reaction conditions may effect introduction of two acyl groups, a cleavage of the *ortho*-methoxy- group, or both.

It has been reported that if the ether and acetyl chloride are dissolved in carbon disulfide, 2,4-dimethoxyacetophenone (m.p. 40°) is obtained.[595]

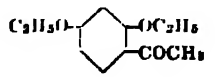
If no solvent is used, and the ether in acetyl chloride is gradually treated with an equivalent amount of aluminum chloride, a 70 per cent yield of 2,4-dimethoxyacetophenone, together with a compound (m.p 145°) is obtained.[596]

The use of two moles each of acetyl chloride and aluminum chloride with one mole of the ether gives the monomethyl ether of diacetylresorcinol (I) (m.p. 121°), soluble in alkali, together with the dimethyl ether of diacetylresorcinol (II) (m.p. 171-172°) insoluble in alkali [597]:





Resorcinol diethyl ether and acetyl chloride in the presence of carbon disulfide and aluminum chloride were reacted by Gattermann and coworkers,[598] who obtained a diethoxyacetophenone (m.p. 67-68°) of the following structure:



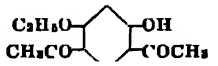
They also obtained the corresponding compound, 1,4-diethoxypropiophenone (m.p. 133°) from propionyl chloride and the ether.

The acetylation of the diethyl ether was reported by Claus and Huth,[599] however, to result in the formation of a dihydroxyacetophenone, m.p. 178°. According to a number of authorities, the melting point of resacetophenone has been reported to be 141-147°; that of 2-acetohydroquinone, 202°; and that of 4-acetopyrocatechol, 116°. The composition and molecular weight of the compound obtained by Claus and Huth was reported to be identical with that of resacetophenone, and it was sug-

[595] F. Sachs and V. Herold, *Ber.*, **40**, 2724 (1907); *cf.* F. Mauthner, *J. prakt. Chem.*, **119**, 311-314 (1928); *C. Z.*, 1928, II, 1202; *Brit. Chem. Abs.*-A, 1014 (1928).
[596] C. Kuroda and T. Matsukuma, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **18**, 51-60 (1932); *Brit. Chem. Abs.*-A, 288 (1932).
[597] F. Mauthner, *J. prakt. Chem.*, **119**, 311-314 (1928); *C. Z.*, 1928, II, 1202; *Brit. Chem. Abs.*-A, 1014 (1928).
[598] L. Gattermann, R. Ehrhardt, and H. Maisch, *Ber.*, **23**, 1190-1210 (1890).
[599] A. Claus and M. Huth, *J. prakt. Chem.*, **53**, (2), 39-43 (1896); *J. Chem. Soc. Abs.*, 1896, I 227

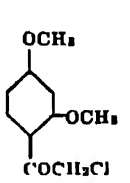
gested that the new compound was an isomeric resacetophenone. Eijkman and co-workers [600] showed that the compound prepared by Claus and Huth was identical with 2,4-dihydroxy-1,5-diacetylbenzene, m.p. 183°

Since cleavage of both alkyl groups in acetylation of resorcinol ethers is unusual, the problem was reattacked by Mauthner.[597] The work of Gattermann and co-workers was confirmed, *i.e.*, the production of asymmetric monoacetodiethyl ether of resorcinol from molecular amounts of acetyl chloride, aluminum chloride, and diethyl ether of resorcinol. With two moles each of acetyl chloride and aluminum chloride, however, there was formed only the monoethyl ether of diacetoresorcinol (m.p. 109°) of the structure:



The compound reported by Claus and Huth could not be obtained.

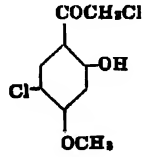
In the reaction of chloroacetyl chloride with resorcinol dimethyl ether, Kunckell [601] obtained what he reported to be a dimethoxy- compound, 2,4-dimethoxy-ω-chloroacetophenone, m.p. 104°:



However, Tutin [602] reports that he obtained the same compound, but that it had a melting point of 96°. Using the same proportion of reactants, but applying heat in order to complete the reaction, von Auwers and Pohl [603] obtained a mono-ether, 2-hydroxy-4-methoxy-ω-chloroacetophenone (m.p. 116°) in 86 per cent yield. Here one of the methoxy- groups had been hydrolyzed. Later, Tambor and DuBois [604] dissolved 40 g of aluminum chloride into the same amount of chloroacetyl chloride. To this, with ice-cooling, he added 50 g of resorcinol dimethyl ether in 100 g of carbon disulfide. He allowed the entire mixture to stand for three days at the ordinary temperature with exclusion of air. The product that he obtained was reported to be the dimethoxy compound, ω-chlororesacetophenone dimethyl ether, m.p. 119°. The melting point of this compound is almost the same as that of the monoether obtained by von Auwers and Pohl. However, there was found to be a great depression of melting point when the two compounds were mixed. Tutin's so-called dimethoxy-compounds which melted at 96° must have been a mixture of the mono- and dimethyl ethers.

[600] J. F. Eijkman, F. Bergema, and J. T. Henrard, *Chem. Weekblad*, **2**, 59-72, 79-93 *C. Z.*, 1905 (I), 814.
[601] F. Kunckell, *Ber. dtsch. pharm. Ges.*, **23**, 188-227 (1890); *C. Z.*, 1913, I, 1789.
[602] F. Tutin, *J. Chem. Soc.*, **97**, 2513 (1910).
[603] K. v. Auwers and P. Pohl, *Ann.*, **405**, 264 (1914).
[604] J. Tambor and E. M. DuBois, *Ber.*, **51**, 748-751 (1918); *J. Chem. Soc. Abs.*, **114**, 395 (1918)

Using chlororesorcinol dimethyl ether with chloroacetyl chloride, von Auwers and Pohl [605] obtained 2-hydroxy-4-methoxy-5-chloro-ω-chloroacetophenone:

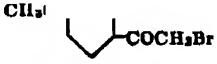


(m.p. 178.5-180°) in 66 per cent of theoretical yield. The presence of chlorine in the ring obviously did not influence the normal course of the reaction.

With bromoacetyl bromide and resorcinol dimethyl ether there have likewise been reported results which are at variance. Blom and Tambor [606] dissolved equal proportions of the ether and bromoacetyl bromide in carbon disulfide and treated the solution with a proportionate amount of aluminum chloride. The reaction mixture was subsequently gently heated on the water-bath for one to two hours. They reported that the compound thus obtained by them was α-bromoresacetophenone dimethyl ether, m.p. 102°.

von Auwers and Pohl [607] repeated the preparation, but were unable to obtain this compound. They found the product to be mostly α-bromo-2-hydroxy-4-methoxyacetophenone. A chloride also appeared to be formed during the reaction. Evidently a part of the bromine had been replaced by chlorine. Subsequently, von Auwers and Müller [608] obtained a good yield of 1-hydroxy-5-methoxy-2-(α-chloropropionyl)-phenol (m.p. 84-85°) by dissolving 15 g of the ether in the same volume of carbon disulfide, adding 15 g of aluminum chloride under ice-cooling, and then 23 g of α-bromopropionyl bromide, disolved in carbon disulfide, at room temperature. The mixture was heated on a water-bath until hydrogen chloride ceased to be evolved. Here, too, the α-bromine was replaced by chlorine.

A year later, Tambor and DuBois [604] again studied the reaction of bromoacetyl bromide with resorcinol dimethyl ether. No heat was applied during the reaction, and the addition of the ether to the bromide was done with ice-cooling. This time, in order to avoid the presence of any chlorine during the reaction, aluminum bromide was used as catalyst. Even under these careful conditions, no dimethoxy- compound was obtained. The product was ω-bromoresacetophenone monomethyl ether,



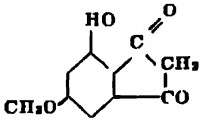
[605] K. v. Auwers and P. Pohl, *Ann.*, 405, 275 (1914).
[606] A. Blom and J. Tambor, *Ber.*, 38, 3590-3592 (1905).
[607] K. v. Auwers and P. Pohl, *Ann.*, 405, 284 (1914).
[608] K. v. Auwers and W. Müller, *Ber.*, 50, 1173-1174 (1917).

It melted at 92°. Apparently it was not possible to obtain α-bromoresacetophenone dimethyl ether in the pure state.

Using 25 g of chloroacetyl chloride and 8 g of diethyl resorcinol ether with 40 g of aluminum chloride and 40 g of carbon disulfide, Kunckell [609] obtained the diacylated compound, bis(chloroacetyl)resorcinol diethyl ether, m.p. 106°.

Oxalyl chloride with resorcinol dimethyl ether and aluminum chloride gives 2,4,2',4'-tetramethoxybenzophenone.[610]

Malonyl chloride was reacted with resorcinol dimethyl ether by Black, Shaw, and Walker.[611] During twenty minutes, 13.5 g of aluminum chloride was added in small portions to a mixture of 7 g of the ether and 7 g of the malonyl chloride in 60 cc of dry nitrobenzene. This solvent was found to give better results than carbon disulfide. The temperature rose to about 40° and the reaction was completed by gradually warming the mixture to 70° during one hour with exclusion of moisture. There was obtained a 30 per cent yield of 7-hydroxy-5-methoxyindan-1,3-dione (m.p. 217°):



In the same way methylmalonyl chloride gave 7-hydroxy-5-methoxy-2-methylindan-1,3-dione, m.p. 225-226°. With ethylmalonyl chloride there was obtained 7-hydroxy-5-methoxy-2-ethylindan-1,3-dione. When *n*-propylmalonyl chloride was reacted with resorcinol dimethyl ether by the same general procedure, there was secured an 84 per cent yield of 7-hydroxy-5-methoxy-2-*n*-propylindan-1,3-dione together with a small amount (about 5 per cent) of the dimethylated condensation product.

Demethylation of one of the methoxy- groups occurred readily during the condensation of resorcinol dimethyl ether with the malonyl chloride; the other methoxy- group, however, was not affected even at raised temperatures or upon prolonged heating. Only the *ortho*-methoxy- group was demethylated; the *para*- group could not be attacked.

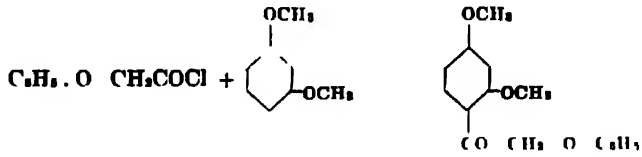
Krafft [612] reacted 2 parts of palmitoyl chloride and 3 parts of resorcinol dimethyl ether with 2 parts of aluminum chloride in the cold and in the absence of a diluent. He allowed the reaction mixture to stand for three to four days at a temperature slowly increasing from 40-100°. He obtained 2,4-dimethoxypalmitophenone, m.p. 63.5° and b_{15} 289-290°.

Using benzoyl chloride, König and Kostanecki [613] obtained 2,4-dimethoxybenzophenone (m.p. 87-88°) from resorcinol methyl ether in the presence of aluminum chloride. Shriner and Damschroder [614] reacted

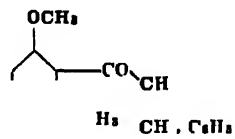
[609] F. Kunckell, *Ber. dtsch. pharm. Ges.*, 23, 183-227 (1890); *C. Z.*, 1913, I, 1769.
[610] H. Staudinger, E. Schlenker, and H. Goldstein, *Helv. chim. acta*, 4, 334-342 (1921); *C. A.*, 15, 3445.
[611] R. Black, H. Shaw, and T. K. Walker, *J. Chem. Soc.*, 272-279 (1931); *Brit. Chem. Abs.*-A, 487 (1931).
[612] F. Krafft, *Ber.*, 21, 2265-2271 (1888).
[613] B. König and St. v. Kostanecki, *Ber.*, 39, 4027-4031 (1906).
[614] R. L. Shriner and R. E. Damschroder, *J. Am. Chem. Soc.*, 60, 894-896 (1938).

α-bromo-β-phenylpropionyl chloride with resorcinol dimethyl ether in the presence of carbon disulfide and aluminum chloride. The reaction mixture was heated for about twenty hours so that cleavage of the *o*-methoxy- group occurred; otherwise normal acylation took place

Upon reacting phenoxyacetyl chloride with resorcinol dimethyl ether and anhydrous aluminum chloride, normal substitution occurs, with the formation of 2,4-dimethoxyphenyl phenoxymethyl ketone (m p. 118 5°) according to the reaction [615]:



With cinnamoyl chloride, Simonis and Danischewski [616] report the preparation of 2,6-dimethoxychalcone from resorcinol dimethyl ether with aluminum chloride and carbon disulfide.

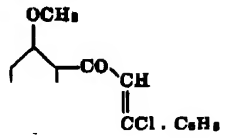


It melted at 80°, and the yield was 78 per cent of theoretical. From resorcinol diethyl ether and cinnamoyl chloride, Simonis and Lear [617] similarly obtained the corresponding ethoxy- compound, reported as 2,6-diethoxychalcone (m.p. 90.5°) in 60 per cent yield. According to von Auwers and Risse,[618] repetition of this work shows that the products are 2,4-dimethoxychalcone and 2,4-diethoxychalcone.

Bodani and co-workers [619] report that in the reaction of cinnamoyl chloride with 1,3-dialkoxybenzenes, the entering acyl group does not go *ortho*- to both alkoxy- groups. He secured dialkyl ethers of resorcinol substituted in the 4-position. This corresponds to other acylations of resorcinol ethers, in which *o*-, *p*-substitution is obtained.

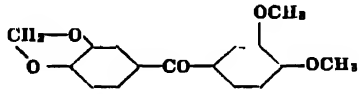
Simonis and Danischewski [616] stated that when phenylpropiolic acid chloride is used, the entering acyl group goes *ortho*- to both substituents. Demethylation of the condensate resulting from resorcinol dimethyl ether and phenylpropiolic acid in the presence of aluminum chloride (effected by addition of another mole of the catalyst) was said to result in formation of 6-methoxy-2-hydroxy-β-chlorochalcone,

[615] R. Stoermer and P. Atenstädt, *Ber.*, 35, 3500-3505 (1902).
[616] H. Simonis and S. Danischewski, *Ber.*, 39, 3014-3019 (1926); *Brit. Chem. Abs.*-A, 154 (1927).
[617] H. Simonis and C. Lear, *Ber.*, 39, 2008-2013 (1926); *C. A.*, 21, 1255.
[618] K. v. Auwers and E. Risse, *Ber.*, 64, 2216-2222 (1931).
[619] D. C. Bodani, V. V. Bodani, and T. S. Wheeler, *Current Sci.*, 6, 604 (1938); *C. A.*, 32, 8381



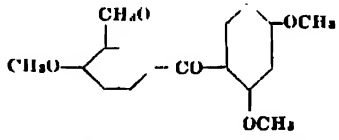
melting at 95°. The yield was 42 per cent. Here the further use of aluminum chloride not only resulted in demethylation, but also in the introduction of the HCl present into the triple bonds of the propiolic radical. However, in repeating this work, von Auwers and Risse [618] were unable to obtain a chlorine-containing compound as the product of the reaction of phenylpropiolic acid with resorcinol methyl ether. Instead, they secured a substance melting at 135-136°, which was not identified.

Perkin and Weizmann [617a] condensed piperonyl chloride and resorcinol dimethyl ether in carbon disulfide in the presence of aluminum chloride. They heated the reaction mixture on a water-bath for five hours and obtained the corresponding dimethoxy- ketone (m.p. 141-142°) to which they gave the structure:

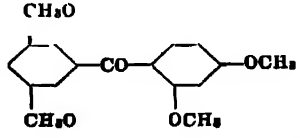


The position of the methoxy- groups as shown here indicates a veratrole, rather than a resorcinol derivative.

Veratroyl chloride and resorcinol dimethyl ether in carbon disulfide with aluminum chloride give 2,4,3′,4′-tetramethoxybenzophenone, m.p. 107°.[618a]



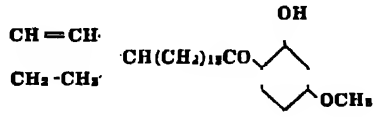
Here the entering group takes the normal course of *o*, *p*- entry. In the same way, 3,5-dimethoxybenzoyl chloride reacts with resorcinol dimethyl ether in the presence of aluminum chloride and carbon disulfide to yield 2,4,3′,5′-tetramethoxybenzene, m.p. 73-74°.[619a]



Chaulmoogryl chloride and the dimethyl ether of resorcinol were reacted by Hinegardner and Johnson.[620] If the ether and chloride were

[617a] W. H. Perkin, Jr., and C. Weizmann, *J. Chem. Soc.*, 89, 1649-1665 (1906).
[618a] B. König and St. v. Kostanecki, *Ber.*, 39, 4027-4031 (1906).
[618b] F. Mauthner, *J. prakt. Chem.*, 87, (ii), 403-409 (1913); *J. Chem. Soc. Abs.*, 104 (1), 632 (1913); *C. A.*, 7, 2344.
[619a] W. S. Hinegardner and T. B. Johnson, *J. Am. Chem. Soc.*, 51, 1503-1509 (1929).

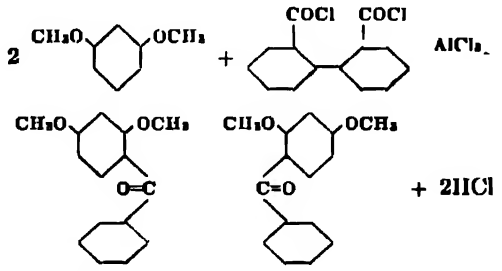
dissolved in carbon disulfide and slowly added to aluminum chloride in carbon disulfide, two products were obtained, 1-chaulmoogryl-2-hydroxy-4-methoxybenzene (m.p. 65°) (I), and 1-chaulmoogryl-2,4-dimethoxybenzene, m.p. 46°.



(I)

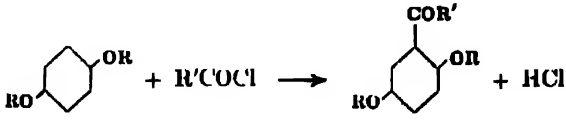
When the aluminum chloride was added to the solution of the ether and acid chloride, and the reaction temperature was kept at 30-35°, only the dimethoxy- compound, in 40 per cent yield, was obtained. An attempt to remove both methyl groups from the resorcinol was unsuccessful. The methyl group *para-* to the entering acyl group could not be removed without decomposing the compound.

Resorcinol dimethyl ether with diphenic acid chloride reacts in the presence of aluminum chloride to give, among other products, some 2,2'-bis(2",4"-dimethoxybenzoyl)biphenyl.[621]



Hydroquinone Ethers

In acylation of hydroquinone ethers, the entering group necessarily goes *ortho-* and *meta-* to the alkoxy- groups. Here both ether groups may be hydrolyzed. Extreme care and low temperatures must be used in order to insure the production of a dialkoxy- ketone .



Hydroquinone dimethyl ether was acetylated by Klages[622] and by Kauffmann and Beisswanger,[623] who secured 2,5-dimethoxyacetophenone. To a mixture of 40 g of aluminum chloride and 40 g of acetyl chloride cooled to −5°, Klages slowly added a solution of 40 g of

[621] P. Bell and F. Bragg, *J. Chem. Soc*, 1938, 1561-1568.
[622] A. Klages, *Ber*, 37, 3996 (1904).
[623] H. Kauffmann and A. Beisswenger, *Ber.*, 38, 789-798 (1905).

hydroquinone dimethyl ether in 120 g of carbon disulfide. The reaction mixture was allowed to remain at room temperature for four hours and then decomposed with ice and dilute HCl. The 2,5-dimethoxyacetophenone was found to be a thick oil, b.p. 156-158° at 15 mm. Kauffmann and Beisswenger used substantially the same procedure except that instead of cooling the mixture of acid chloride and catalyst they warmed it slightly. For this reason they allowed the reaction mixture to stand for only two hours, instead of for four hours as Klages had done. The yield obtained by them was 46 per cent of theoretical. Their product boiled at 155-158° at 14 mm, and was found to solidify to large crystals upon standing, melting at 20-22°. As by-product they also obtained a small amount of the demethylated product, 2-hydroxy-5-methoxyacetophenone.

Kuroda [624] used no solvent in the reaction. Instead, an excess of acetyl chloride was used. The ether was dissolved in the acid chloride and aluminum chloride (in amount equal to the ether) was gradually added, with stirring. As the reaction proceeded, the excess of acetyl chloride was allowed to evaporate, and the reaction mixture became a paste. The 2,5-dimethoxyacetophenone was obtained as an oil. When purified by vacuum distillation, it crystallized and was found to melt at 21-22°. The yield was almost theoretical.

With chloroacetyl chloride, von Auwers and Pohl [625] obtained 2,5-dimethoxy-ω-chloroacetophenone, m.p. 87-88°. To 11 g of the ether in 60 cc of carbon disulfide was added, with cooling, 10 g of aluminum chloride. To this was slowly added 9 g of the acid chloride dissolved in 15 cc of carbon disulfide. The reaction mixture was allowed to stand for three hours. A small amount of the monomethyl compound, 5-methoxy-2-hydroxy-ω-chloroacetophenone (m.p. 81-81.5°) was also formed in the reaction.

In another experiment, von Auwers and Pohl obtained a 65 per cent of theoretical yield of the mono-ether. Here the same procedure and practically the same proportion of reactants was used, except that the reaction mixture was warmed on the water-bath for twenty hours.

In reacting bromoacetyl bromide with hydroquinone dimethyl ether, Tambor [626] allowed the reaction mixture to stand for several days with exclusion of air at ordinary temperature. He secured in the entirely pure state 2,5-dimethoxy-ω-bromoacetophenone, m.p. 91°. No heat was applied during the course of the reaction. The fact that even after standing for several days no cleavage of the methyl group was reported is noteworthy.

Johnson and Hodge [627] report the production of 1,4-dimethoxy-2-propionylbenzene (b.p. 167-169°/13 mm) after heating almost to the boiling point for thirty hours a reaction mixture consisting of 29 g of hydro-

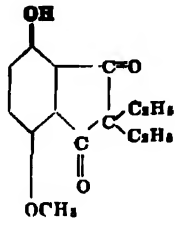
[624] C. Kuroda and T. Matsukuma, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 18, 51-60 (1933); *Brit. Chem. Abs.*-A, 388 (1933).
[625] K. v. Auwers and P. Pohl, *Ann.*, 405, 261 (1914).
[626] J. Tambor, *Ber.*, 44, 3215-3224 (1911).
[627] T. B. Johnson and W. W. Hodge, *J. Am. Chem. Soc.*, 35, 1021 (1913).

quinone dimethyl ether, 24 g of propionyl chloride, 36 g of aluminum chloride and 250 cc of petroleum ether. He obtained 14 g of the pure dimethoxy- ketone. According to Cruickshank and Robinson,[628] this reaction gives an oily product (b.p. 140-190°/2 mm) which is a mixture of partially and completely demethylated ketones.

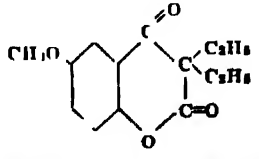
Condensation of hydroquinone dimethyl ether with *n*-valeroyl chloride, by treating with aluminum chloride in carbon disulfide, after four hours gives 2-hydroxy-5-methoxy-*n*-valerophenone, m.p. 62°. Similar reaction with isovaleryl chloride gives 2-hydroxy-5-methoxyisovalerophenone, together with some 2,5-dimethoxyisovalerophenone. With *n*-octoyl chloride the product is 2-hydroxy-5-methoxyoctophenone, m.p 45°.[628]

Palmitoyl chloride was reacted with hydroquinone dimethyl ether in the presence of carbon disulfide and aluminum chloride by Kauffmann and Grombach.[629] No external heat was applied, and the reaction mixture was allowed to stand for twelve hours. The yield of palmitoyl hydroquinone dimethyl ether $(CH_3O)_2C_6H_3.COC_{15}H_{31}$ (m.p. 44°) was 78 per cent of theoretical. Johnson and Kohmann [630] report the easy production of 37 g of the dimethyl ether of myristylhydroquinone (m.p. 51-52°) from 15 g of the ether, 26 g of myristyl chloride and 16 g of aluminum chloride Petroleum ether was used as diluent.

Diethylmalonyl chloride and hydroquinone dimethyl ether in carbon disulfide solution were reacted in the presence of aluminum chloride by Freund and Fleischer.[631] They obtained 4-hydroxy-7-methoxy-2,2-diethyl-1,3-indandione (m.p. 105-106°)



and the corresponding dimethoxy- compound, m.p. 159-161°. They also secured, as one of the products, an oil (b.p. 200°/15 mm), which was identified as 3-diethyl-6-methoxybenzotetronic acid,

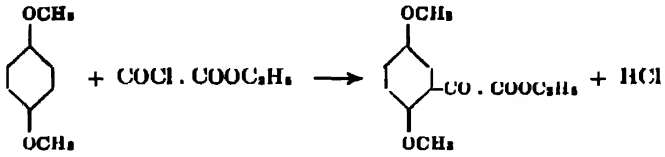


[628] J. H. Cruickshank and R. Robinson, *J. Chem Soc*, 1938, 2064-2071.
[629] H. Kauffmann and A. Grombach, *Ann.*, 344, 67-89 (1906).
[630] T. B. Johnson and E. F. Kohmann, *J. Am. Chem Soc.*, 36, 2159-2166 (1914).
[631] M. Freund and K. Fleischer, *Ann.*, 409, 208-290 (1915).

which is an isomer of 4-hydroxy-7-methoxy-2,2-diethylindandione.

Oxalyl chloride with hydroquinone dimethyl ether and aluminum chloride gives 2,5,2',5'-tetramethoxybenzophenone.[632]

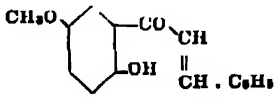
Kauffmann and Grombach[629] reacted ethyl chloroglyoxylate with hydroquinone dimethyl ether according to the equation:



They secured ethyl (2,5-dimethoxyphenyl)glyoxylate (m.p. 38°) after allowing the reaction mixture consisting of 12 g of the ether, 10 g of the acid chloride, 12 g of carbon disulfide and 12 g of aluminum chloride to stand for about 3 hours.

Kauffmann and Grombach[633] also reacted benzoyl chloride with hydroquinone dimethyl ether, obtaining benzoylhydroquinone dimethyl ether (m.p. 51°) in 78 per cent of theoretical yield. To a solution of 50 g of the ether and 50 g of benzoyl chloride in 50 g of carbon disulfide, they gradually added, with ice-cooling, 50 g of aluminum chloride. They allowed the reaction mixture to stand for 48 hours before decomposition with ice and isolation of the reaction products. As a by-product there was also obtained about a 10 per cent yield of benzoylhydroquinone monomethyl ether, m.p. 78°.

The reaction of cinnamoyl chloride with hydroquinone dimethyl ether was studied by Simonis and Danischewski,[634] who dissolved 13.8 g of the ether and 16.6 g of the acid chloride in three times the amount of carbon disulfide and slowly treated the solution, with cooling, with 13.4 g of aluminum chloride. The reaction mixture was warmed at 50° for three hours under reflux. They obtained 2,5-dimethoxychalcone, $(CH_3O)_2$-$C_6H_3.CO.CH{:}CH.C_6H_5$ (m.p. 43°) in 75 per cent yield. Addition of more aluminum chloride to the reaction mixture resulted in cleavage of the o-methoxy- group and the consequent production of the mono-ether, 5-methoxy-2-hydroxychalcone,



which melts at 49°.

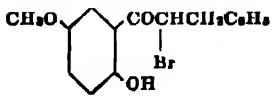
When Simonis and Lear[635] reacted hydroquinone diethyl ether with cinnamoyl chloride, they could not obtain the diethoxy- compound. The use of even 1 mole of aluminum chloride resulted in hydrolysis of the

[632] H. Staudinger, E. Schlenker, and H. Goldstein, *Helv. chim. acta*, 4, 334-342 (1921); *C. A.*, 15, 3445.
[633] H. Kauffmann and C. Grombach, *Ber.*, 38, 794-801 (1905).
[634] H. Simonis and S. Danischewski, *Ber.*, 59, 2014-2019 (1926); *Brit. Chem. Abs.*-A, 154 (1927).
[635] H. Simonis and C. Lear, *Ber.*, 59, 2008-2013 (1926); *C. A.*, 21, 1255.

o-ethoxy- group. The only product obtained by them was 5-ethoxy-2-hydroxychalcone, m.p. 83°.

Phenylacetyl chloride was reacted with hydroquinone dimethyl ether by Kauffmann and Grombach.[636] They used equal amounts by weight of the ether, acid chloride, carbon disulfide and aluminum chloride and allowed the reaction mixture to stand for twelve hours before isolating the reaction product, 2,5-dimethoxydesoxybenzoin, m.p. 49°. The yield was 50 per cent of theoretical.

α-Bromo-β-phenylpropionyl chloride and hydroquinone dimethyl ether in carbon disulfide with aluminum chloride yield 2-hydroxy-5-methoxyphenyl α-bromo-β-phenylethyl ketone:



The reaction mixture was warmed on an oil bath and stirred for from eight to ten hours; heating was continued for ten to twelve hours to insure the cleavage of the *o*-methoxy- group.[637]

Alkoxy-substituted acid chlorides have been condensed with hydroquinone dimethyl ether. König and Kostanecki[638] condensed veratroyl chloride with hydroquinone dimethyl ether in the presence of carbon disulfide and aluminum chloride. They allowed the reaction mixture to stand for 48 hours, and obtained 2,5,3',4'-tetramethoxybenzophenone, m.p. 101-102°.

Again, dimethyl ether of hydroquinone carboxylic acid chloride (dimethyl gentisic acid chloride) was dissolved with hydroquinone dimethyl ether in carbon disulfide and aluminum chloride was added gradually with ice-cooling. After the reaction mixture had stood for several hours it was decomposed, and from it Kauffmann and Grombach[639] isolated 2,5,2',5'-tetramethoxybenzophenone, $(CH_3O)_2C_6H_3 \cdot CO \cdot C_6H_3(OCH_3)_2$, m.p. 109°.

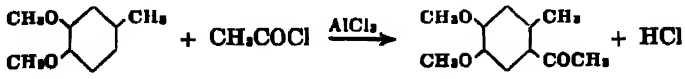
Ethers of Substituted Dihydroxy- Phenols

In a recent study of quinol derivatives, several alkylated hydroquinone dimethyl ethers were acylated.[640] Addition of 2,5-dimethoxy-*n*-propylbenzene to an ice-cold solution of acetyl chloride and aluminum chloride after eight or nine hours gives 2-hydroxy-5-methoxy-4-*n*-propylacetophenone, b.p. 150-155°/1 mm. 2,5-Dimethoxy-*n*-amylbenzene, as well as the iso-amyl isomer, have been similarly reacted with *n*-octoyl chloride to give 2-hydroxy-5-methoxy-4-*n*-amyloctophenone (m.p. 42°) and 2-hydroxy-5-methoxy-4-iso-amyloctophenone (a dark oil), respectively.

Homocatechol dimethyl ether was condensed with acetyl chloride by

[636] H. Kauffmann and A. Grombach, *Ann.*, 344, 65 (1906).
[637] R. L. Shriner and R. E. Damschroder, *J. Am. Chem. Soc.*, 60, 894-896 (1938).
[638] B. König and St. v. Kostanecki, *Ber.*, 39, 4027-4031 (1906).
[639] H. Kauffmann and A. Grombach, *Ann.*, 344, 74 (1906)
[640] J. H. Cruickshank and R. Robinson, *J. Chem. Soc.*, 2064-2071 (1938).

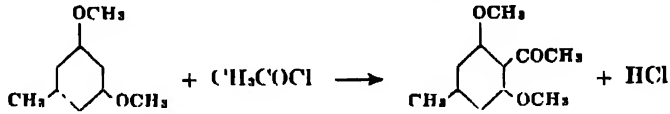
Harding and Weizmann.[641] 4,5-Dimethoxy-2-methylacetophenone (m.p. 68°) was easily obtained according to the following reaction:



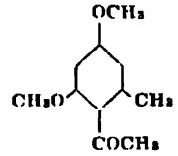
Here, more than the equivalent amount of catalyst was used. For the reaction 30 g of acetyl chloride and 50 g of the ether were dissolved in 200 cc of carbon disulfide and treated with 100 g of aluminum chloride. The mixture was kept at ordinary temperature for 24 hours and then heated for two hours on a water-bath.

According to Stephen and Weizmann,[642] when homocatechol dimethyl ether is condensed with chloroacetyl chloride, using aluminum chloride as catalyst and nitrobenzene as solvent, there is obtained 4,5-dihydroxy-*o*-tolyl chloromethyl ketone, b.p. 187°/14 mm and m.p. 128°. The yield was increased by warming the reaction mixture for eight hours at 40° after all the reactants had gone into solution.

When 1 mole of orcinol dimethyl ether and 1 mole of acetyl chloride dissolved in carbon disulfide was treated with 1 mole of aluminum chloride and the reaction mixture was allowed to stand for 24 hours, Ludwinowsky and Tambor [643] obtained the dimethyl ether of orcinolacetophenone (m.p. 89°) according to the following equation:



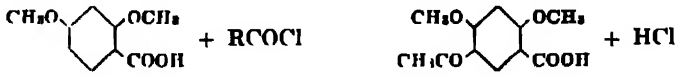
A by-product in this reaction was found to be an isomer, melting at 48° and having the structure [644]:



The substitution of the carboxylic instead of the methyl group in resorcinol dimethyl ether does not vary the progress of the reaction. Thus Liebermann and Lindenbaum [645] dissolved 50 g of the dimethyl ether of resorcylic acid in 750 cc of freshly distilled acetyl chloride and in the course of twenty minutes added 250 g of aluminum chloride. There was rapid reaction with strong evolution of hydrogen chloride; the alu-

[641] V. J. Harding and C. Weizmann, *J. Chem. Soc.*, **97**, 1126-1131 (1910).
[642] H. Stephen and C. Weizmann, *J. Chem. Soc.*, **105**, 1046-1057 (1914).
[643] S. Ludwinowsky and J. Tambor, *Ber.*, **39**, 4037-4041 (1906).
[644] J. Tambor, *Ber.*, **41**, 793-798 (1908).
[645] C. Liebermann and S. Lindenbaum, *Ber.*, **41**, 1607-1619 (1908).

minum chloride was completely dissolved. The liquid was treated with ice water and the reaction product precipitated. After purification and crystallization from ethyl or methyl alcohol there was obtained 2,4-resacetophenone-5-carboxylic acid dimethyl ether (m.p. 231-233°) in 80-90 per cent yield according to the equation:

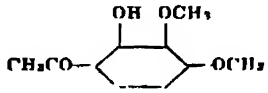


When the diethyl ether of resorcylic acid was similarly treated, the product melted at 190-202°. Analysis showed it to be a mixture of 2,4-resacetophenene-5-carboxylic acid diethyl ether, and the corresponding mono-ether.

Ethers of Trihydroxy- Phenols

Pyrogallol trimethyl ether was reacted with acetyl chloride by Mannich and Hahn [646] who, using 6.3 g of the ether and 3.6 g of acetyl chloride in 16 cc of carbon disulfide with 5.1 g of aluminum chloride, obtained acetyl pyrogallol trimethyl ether, m p 14-15°, and b.p. 165°/12 mm The trimethyl ether as an oil (b p. 140°/10 mm) was also prepared by Kuroda and Nakamura,[647] who obtained an almost theoretical yield by dissolving 5 g of pyrogallol trimethyl ether in 10 cc of acetyl chloride and slowly treating this with 5 g of aluminum chloride. No solvent was used, the excess of acetyl chloride being employed instead.

Perkin and Weizmann [648] secured the dimethyl ether,

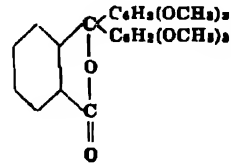


and reported the m p. to be 77°. They dissolved 30 g of pyrogallol trimethyl ether in carbon disulfide and added 16 g of acetyl chloride. The solution was well cooled and gradually mixed with 20 g of aluminum chloride. The mixture was allowed to stand for 24 hours. The authors showed that here the methoxy- group *ortho-* to the ketone group had been hydrolyzed. Repeating the reaction, Bargellini [649] also reported that he obtained 2-hydroxy-3,4-dimethoxyacetophenone, but he gave 83° as the m.p. of the compound.

Perkin and Weizmann [650] reacted pyrogallol trimethyl ether with phthaloyl chloride. One mole of the chloride was dissolved in light petroleum and mixed with 2 moles of the ether. After cooling in ice, finely powdered aluminum chloride was added in small quantities, the total

[646] C. Mannich and F. L. Hahn, *Ber*, 44, 1551 (1911).
[647] C. Kuroda and T. Nakamura *Sci Papers Inst. Phys Chem. Res. Tokyo*, 15, 61-76 (1912) Brit. Chem. Abstracts, A, 388 (1932
[648] W. H Perkin, Jr. and C Weizmann, *J Chem. Soc*, 89, 1654 (1906)
[649] G. Bargellini, *Gazz. chim. ital*, 46, *I*, 249-255 (1916); *C. Z.*, 1916, II, 567.
[650] W. J Perkin, Jr and C Weizmann, *J Chem. Soc*, 89, 1657 (1906).

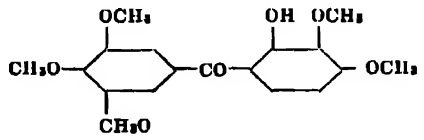
amount used being half that of the combined weights of the chloride and ether. The reaction mixture was allowed to remain for twelve hours in ice water, and was then heated on the water-bath until the evolution of hydrogen chloride had almost stopped. After decanting the solvent and decomposition of the catalyst complex there was obtained, by crystallization from acetic acid, colorless, microscopic needles of bis-(trimethoxyphenyl)-phthalide,



The phthaloyl chloride had reacted as a lactone.

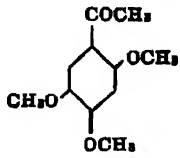
The reaction of pyrogallol dimethyl ether and benzoyl chloride in nitrobenzene with anhydrous aluminum chloride gives 3,4-dihydroxy-5-methoxybenzophenone, m.p. 168-169°.[651]

The chloride of 2-methoxy-*p*-toluic acid was also condensed with pyrogallol dimethyl ether by Perkin and Weizmann.[652] Fifty-four g of the chloride and 50 g of the ether were suspended in carbon disulfide and heated on a water-bath with 56 g of aluminum chloride for about four hours. The product obtained was 4'-methyl-2-hydroxy-3,3',4-trimethoxybenzophenone, $CH_3(OCH_3)C_6H_3.CO.C_6H_2(OH)(OCH_3)_2$ (m.p. 109°) in a 20 g yield. Reacting 3,5-dimethoxybenzoyl chloride with pyrogallol trimethyl ether in the presence of carbon disulfide and aluminum chloride, Mauthner[653] obtained 3,5,3',4'-tetramethoxy-2'-hydroxybenzophenone, m.p. 123-124°. From the trimethyl ether of gallyl chloride and pyrogallol trimethyl ether heated in carbon disulfide solution with aluminum chloride on a water-bath Perkin and Weizmann[654] secured 2-hydroxy-3,4,3',4',5'-pentamethoxybenzophenone, m.p. 133-134°:



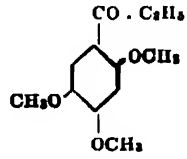
Hydroxyhydroquinone trimethyl ether in carbon disulfide was reacted with acetyl chloride in the presence of aluminum chloride by Reigrodski and Tambor.[655] Equimolecular proportions of the reactants were used, and the reaction mixture was allowed to stand for two days before isolation of the product, 2,4,5-trimethoxyacetophenone, m.p. 102-103°.

[651] F. Mauthner, *J. prakt. Chem.*, 133, 126-128 (1932); *C. A.*, 26, 2441.
[652] W. J. Perkin, Jr. and C. Weizmann, *J. Chem. Soc.*, 89, 1649-1665 (1906).
[653] F. Mauthner, *J. prakt. Chem.*, 87, 408-409 (1913) (II); *J. Chem. Soc. Abs.*, 104, (I), 632 (1913); *C. A.*, 7, 2544.
[654] W. H. Perkin, Jr. and C. Weizmann, *J. Chem. Soc.*, 89, 1665 (1906).
[655] J. Reigrodski and J. Tambor, *Ber.*, 43, 1964-1968 (1910).

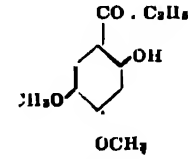


The same reaction was also studied by Bargellini and Avrutin [656] who reported that the 2,4,5-trimethoxy- compound melted at 102° and boiled at 285-290°/33 mm. Kuroda and Matsukoma [657] prepared the compound by dissolving the ether in an excess of acetyl chloride and then gradually treating the solution with aluminum chloride in an amount equal to the ether used. No solvent was used. For 2,4,5-trimethoxyacetophenone they found the m.p. to be 99°.

Bargellini [658] reacted the trimethyl ether of hydroxyhydroquinone with propionyl chloride. He obtained 2,4,5-trimethoxypropiophenone (m.p. 106-108°) and a by-product, the corresponding di-ether. The preparation was repeated by Bargellini and Martegiani,[659] who dissolved 30 g of hydroxyhydroquinone trimethyl ether in carbon disulfide and added 18 g of propionyl chloride and 25 g of aluminum chloride. The reaction mixture was heated on a water-bath. There were obtained 24 g of trimethoxypropiophenone (I) and 11 g of 4,5-dimethoxy-2-hydroxypropiophenone (II), which melts at 124-126°.



(I)



(II)

Benzoyl chloride and hydroxyhydroquinone trimethyl ether were also reacted by Bargellini and Martegiani.[660] By the action of 11 g of aluminum chloride on a solution of 11 g benzoyl chloride in 50 cc of carbon disulfide which had previously been mixed with 11 g of the ether in 50 cc of carbon disulfide they obtained the following:

2,4,5-trimethoxybenzophenone, m.p. 97°
2-hydroxy-4,5-dimethoxybenzophenone, m.p. 106-107°

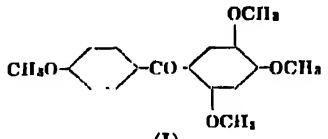
The dimethoxy- compound could also be obtained by heating the corresponding trimethyl ether with aluminum chloride in carbon disulfide.

Reacting hydroxyhydroquinone trimethyl ether with cinnamoyl chloride in carbon disulfide in the presence of aluminum chloride for two hours at room temperature and then for two hours on the water-bath,

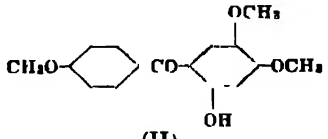
[656] G. Bargellini and G. Avrutin, *Gazz. chim. ital.*, 40, II, 342-346 (1910); *C. A.*, 5, 2098 (1911).
[657] C. Kuroda and T. Matsukoma, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 18, 51-60 (1932); *C. Z.*, 1932, I, 3170.
[658] G. Bargellini, *Atti accad. Lincei, (5)* 20, I, 22-26; *C. Z.*, 1911, I, 981.
[659] G. Bargellini and E. Martegiani, *Atti accad. Lincei, (5)*, 20, II, 18-25; *C. Z.*, 1911, II, 1026.
[660] G. Bargellini and E. Martegiani, *Atti accad. Lincei, (5)*, 20, II, 183-190; *C. Z.*, 1911, II, 1788-1789.

Bargellini and Finkelstein [601] obtained the chalcone, 2,4,5-$(CH_3O)_3C_6H_2$-$CO.CH{:}CH.C_6H_5$. If, however, the heating of the mixture of hydroxyhydroquinone trimethyl ether, cinnamyl chloride, and aluminum chloride is prolonged to ten or twelve hours, the principal product (m.p. 127-128°) was what they assumed to be the product of a disubstitution. The compound had probably been substituted at the olefinic linkage of the double bond.

From anisoyl chloride and hydroxyhydroquinone trimethyl ether in the presence of aluminum chloride, Bargellini and Martegiani [600] obtained 2,4,5,4′-tetramethoxybenzophenone (I) (m.p. 122-124°) and 4,5,4′-trimethoxy-2-hydroxybenzophenone (II), m.p. 127-128°.

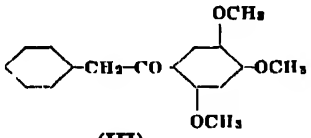


(I)

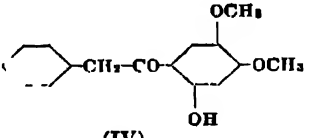


(II)

Likewise, in the similar condensation of hydroxyhydroquinone trimethyl ether with phenylacetyl chloride they obtained the tri- and dimethoxy products, 2,4,5-trimethoxydesoxybenzoin (III) (m.p. 76-77°) and 4,5-dimethoxy-2-hydroxydesoxybenzoin, m.p. 94° (IV).



(III)



(IV)

Phloroglucinol trimethyl ether was reacted with acetyl chloride by Friedlaender and Schnell.[602] They dissolved the ether in about 15 parts of petroleum ether and added somewhat more than the calculated amount of acetyl chloride. While gently heating the solution on the water-bath they gradually added aluminum chloride. The main product of the reaction was a mixture of the trimethyl ether of phloroacetophenone (m.p. 97-98°) together with a lesser amount of the dimethoxy- compound, $C_6H_2OH(OCH_3)_2COCH_3$, m.p. 85-88°.

Kuroda and Matsukoma [603] performed the reaction without using a solvent, employing, instead, an excess of acetyl chloride. They secured an almost theoretical yield of the trimethoxy- compound, 2,4,6-trimethoxyacetophenone, and reported its melting point to be 102°.

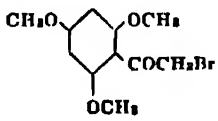
According to Gulati and Venkataraman [604] the condensation of phloroglucinol trimethyl ether with acetyl chloride for the production of 2,4,6-

[601] G. Bargellini and M. Finkelstein, *Gazzetta*, 42, (ii), 417-426 (1912); *J. Chem. Soc. Abs.*, 104, (I), 59 (1913); *C. A.*, 7, 1713.
[602] P. Friedlaender and L. C. Schnell, *Ber.*, 30, 2150-2153 (1897).
[603] C. Kuroda and T. Matsukoma, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 18, 51-60 (1933); *C. Z.*, 1932, I, 2170.
[604] K. C. Gulati and K. Venkataraman, *J. Chem. Soc.*, 357-369 (1936); *C. A.*, 30, 2966.

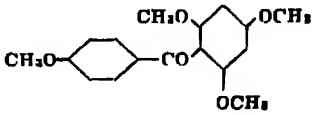
trimethoxyacetophenone proceeds best at −5° to −10°, with the aluminum chloride being added to the reaction mixture during three hours.

In reacting phloroglucinol trimethyl ether with chloroacetyl chloride in the presence of aluminum chloride, Friedlaender and Schnell [665] used petroleum ether as solvent. When all the reactants had dissolved, the solvent was distilled off, and the residue was heated for three more hours. They secured dimethoxy-*o*-hydroxy-ω-chloroacetophenone, $C_6H_2.(OH)\text{-}(OCH_3)_2.COCH_2Cl$, m.p. 142-144°.

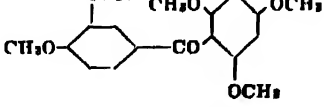
Dumont and Tambor [666] reacted bromoacetyl bromide with phloroglucinol trimethyl ether. A solution of 16 g of the ether and 20 g of the bromide in a little carbon disulfide was gradually treated with 20 g of aluminum chloride and then allowed to stand at ordinary temperature After removal of solvent and decomposition of the reaction complex with ice and dilute HCl, the ketone was secured by crystallization from alcohol The α-bromophloroacetophenone trimethyl ether obtained melted at 126° and was assigned the following structure:



Kostanecki and Tambor [667] reacted anisoyl chloride and phloroglucinol trimethyl ether in carbon disulfide with aluminum chloride They secured 2,4,6,4′-tetramethoxybenzophenone, m.p. 146°:



Using veratroyl chloride instead of anisoyl chloride in the foregoing reaction, they secured 2,4,6,3′,4′-pentamethoxybenzophenone,

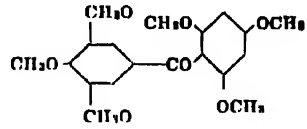


melting at 157°. Mauthner [668] reacted 3,5-dimethoxybenzoyl chloride with phloroglucinol trimethyl ether in carbon disulfide solution in the presence of aluminum chloride. He obtained a pentamethoxybenzophenone melting at 132-133°.

By treatment of trimethylgalloyl chloride and phloroglucinol tri-

[665] P. Friedlaender and L. C. Schnell, *Ber.*, 30, 2150-2153 (1897).
[666] H. Dumont and J. Tambor, *Ber.*, 43, 1969-1971 (1910)
[667] St. v. Kostanecki and J. Tambor, *Ber.*, 39, 4025-4034 (1906).
[668] F. Mauthner, *J. prakt. Chem.*, 87, (ii), 403-409 (1913); *J. Chem. Soc. Abs.*, 104, (I), 632 (1913), *C. A.*, 7, 2644.

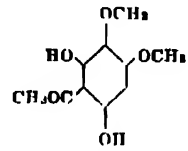
methyl ether in carbon disulfide solution with aluminum chloride Kostanecki and Tambor [669] obtained 2,4,6,3',4',5'-hexamethoxybenzophenone (m.p. 122°):



Ethers of Substituted Trihydroxy- Phenols

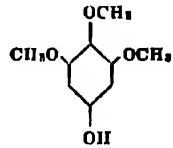
Antiarol was reacted with acetyl chloride in nitrobenzene solution in the presence of aluminum chloride. Chapman and co-workers [670] isolated two substances in small yield. The first (m.p. 92-93°) gave analytical results corresponding to formula (I), and the second (m.p. 160-161°) was found to be probably (II).

(I)



(II)

In both cases the original hydroxy- group of antiarol,



was not affected, but demethylation of one of the methoxy- groups resulted.

Ethers of Tetrahydroxy- Phenols

When Bargellini and Bini [671] and, later, Bargellini [672] treated 1,2,3,5-tetramethoxybenzene with acetyl chloride in the presence of aluminum chloride in carbon disulfide solution they secured:

(1) the tetramethoxyacetophenone, m.p. 43-45°
(2) 2,3,4,6-tetrahydroxyacetophenone trimethyl ether, m.p. 105-107°
(3) 2,3,4,6-tetrahydroxyacetophenone dimethyl ether, m.p. 162-163°
(4) 2-hydroxy-3,4,6-trimethoxyacetophenone, m.p. 112-113°

[669] St. v. Kostanecki and J. Tambor, *Ber.*, **39**, 4023-4024 (1906).
[670] E. Chapman, A. G. Perkin, and R. Robinson, *J. Chem. Soc.*, 3020 (1927).
[671] G. Bargellini and L. Bini, *Atti accad. Lincei*, 1910, (v), **19**, ii, 595-600; *J. Chem. Soc. Abs.*, 1911, I, 211.
[672] G. Bargellini, *Gazzetta*, 1919, **49**, II, 47-63; *J. Chem. Soc. Abs.*, 845 (I) (1919); G. Bargellini, *Atti X° congr. intern. chim.*, **3**, 82 (1939); *C. A.*, **34**, 1018.

Chapman and co-workers [670] repeated the experiment and secured:

(1) cream-colored crystals, m.p. 177-178°
(2) yellow prisms, m.p. 111-112°
(3) brownish-yellow crystals, m.p. 162-163°
(4) 2,3,4,6-tetramethoxyacetophenone, m.p. 53-54°

Kuroda [673] performed the reaction without using a solvent, employing instead an excess of acetyl chloride. Two grams of 1,2,3,5-tetramethoxybenzene in 4 g of acetyl chloride was gradually treated with 2 g of aluminum chloride. In about twenty minutes the product became semisolid, and ice was added. 2,3,4,6-Tetramethoxyacetophenone then crystallized in long, colorless needles. The yield was almost theoretical Kuroda reported that the *oxime* of the tetramethoxyacetophenone melted at 53-54°.

Using propionyl chloride with carbon disulfide and aluminum chloride, Bargellini [674] secured 2,3,4,6-tetrahydroxypropiophenone trimethyl ether, $OH \cdot C_6H(OCH_3)_3CO \cdot C_2H_5$ (m.p. 124-126°). Under similar conditions, with benzoyl chloride, he obtained 2,3,4,6-tetrahydroxybenzophenone trimethyl ether, $OH.C_6H(OCH_3)_3CO.C_6H_5$, m.p. 87-89°.

Ethers of Polynuclear Phenols and Acid Chlorides

Naphthyl Ethers

Reacting various α- and β-naphthyl ethers with acyl chlorides in the presence of aluminum chloride with carbon disulfide as diluent, Gattermann [675] reported the preparation of the following compounds:

acetyl-α-naphthyl methyl ether, m.p. 71-72° (the acetyl group probably being *para*)
propionyl-α-naphthyl methyl ether, m.p. 58°
acetyl-α-naphthyl ethyl ether, m.p. 78-79°
benzoyl-α-naphthyl ethyl ether, m.p. 57-58°
acetyl-β-naphthyl ethyl ether, m.p. 62-63°

In repeating Gattermann's work, Witt and Braun [676] found that in the reaction between the naphthyl ethers and acyl chlorides there is also a hydrolysis of the alkoxy- group, so that in the case of the reaction of acetyl chloride and α-naphthyl ethyl ether, for example, there are formed 4-acetyl-α-naphthol (m.p. 198°) a diacetyl-α-naphthol (m.p. 140°), and the 4-acetyl-α-naphthyl ether, m.p. 78-79°. The authors pointed to the formation of these products as a proof that aluminum chloride, under casual conditions, may hydrolyze the ether, and then cause the introduction of an acetyl group into the 2- or 4-position, or even the introduction of two acetyl groups.

[673] C. Kuroda, *J. Chem. Soc.*, 1930, 767.
[674] G. Bargellini, *Gazzetta*, 45, i, 85-93 (1915); *J. Chem. Soc. Abs.*, 108, (I), 81 (1915).
[675] L. Gattermann, R. Ehrhardt, and H. Maisch, *Ber.*, 22, 1129-1133 (1889); *J. Chem. Soc. Abs.*, 56, 963 (1889); *Ber.*, 23, 1190-1210 (1890); *J. Chem. Soc. Abs.*, 58, (II), 963 (1890).
[676] O. N. Witt and O. Braun, *Ber.*, 47, 3215-3232 (1914); *J. Chem. Soc. Abs.*, 1915, I, 414.

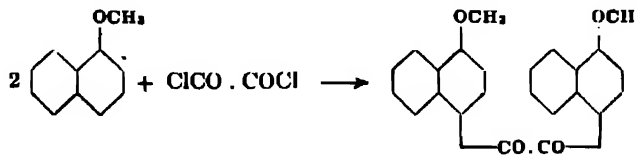
In the condensation of nerolin (β-naphthyl methyl ether) with acetyl chloride by the Friedel-Crafts reaction in benzene, there was obtained 3-acetyl-β-naphthol (m.p. 64-65°) and a diacetyl-β-naphthol, probably 3,6-diacetyl-β-naphthol, as well as the compound obtained by Gattermann, acetyl-β-naphthyl methyl ether, m.p. 57.5-58°.

This hydrolysis of naphthyl ethers in the presence of aluminum chloride had previously been studied by Hartmann and Gattermann [677] who reported that acetyl-α-naphthol ethyl ether, for example, was readily hydrolyzed to acetyl-α-naphthol.

Because of the uncertainty of the products obtained by aluminum chloride hydrolysis, Fries [678] investigated the constitution of the compound which was designated by Witt and Braun as 3-acetyl-β-naphthol. Direct comparison of this substance with 2-hydroxy-α-naphthyl methyl ketone indicated that these compounds were identical. Later [679] the 2-hydroxy-3-naphthyl methyl ketone was synthesized, and it was found to differ completely from the product reported by Witt and Braun, which must therefore be regarded as 2-hydroxy-α-naphthyl methyl ketone. The unhydrolyzed product, 2-methoxy-α-naphthyl methyl ketone (m.p. 58°), was also conveniently obtained by the action of acetyl chloride and aluminum chloride on β-naphthyl methyl ether. (Compare with Gattermann [680] and Witt and Braun.[676])

Dichloroacetyl chloride was reacted with α-naphthyl methyl ether by Kunckell and Johannssen,[681] who reported the production of a dichloroacetyl-α-naphthyl methyl ether, m.p. 100°. No product was secured when β-naphthyl methyl ether was used.

Oxalyl chloride with aluminum chloride in carbon disulfide reacts normally with α-methoxynaphthalene to give the diketone, 1,1'-dimethoxy-4,4'-binaphthoyl.[682] The diketone is obtained in 60 per cent of theoretical yield, according to the reaction:

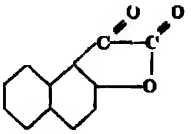


The formation of the preceding diketone, together with a monoketone, bis-(4-methoxy-α-naphthyl) ketone, $CH_3.O.C_{10}H_6.CO.C_{10}H_6.O.CH_3$, has also been reported.[683]

Condensation with β-naphthol ethers, however, does not proceed analogously.[682,683] The product of the reaction of 2-methoxynaphthalene

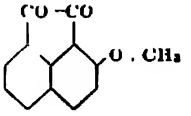
[677] C. Hartmann and L. Gattermann, *Ber.*, 25, 3531-3534 (1892); *J. Chem. Soc. Abs.*, 1893, I, 152.
[678] K. Fries, *Ber.*, 54, 709-714 (1921); *J. Chem. Soc. Abs.*, 120 (I), 422 (1921).
[679] K. Fries and K. Schimmelschmidt, *Ber.*, 58, 2835-2845 (1925); *Brit. Chem. Abs.*-A, 294 (1926).
[680] L. Gattermann, R. Ehrhardt, and H. Maisch, *Ber.*, 23, 1199-1210 (1890); *J. Chem. Soc. Abs.*, 58 (II), 963 (1890).
[681] F. Kunckell and F. Johannssen, *Ber.*, 31, 169-172 (1898).
[682] H. Staudinger, E. Schlenker and H. Goldstein, *Helv. chim. acta*, 4, 334-342 (1921); *C. A.*, 15, 3445.
[683] M. Giua, *Gazz. chim. ital.*, 47 (I), 51-57 (1917); *C. A.*, 12, 1169.

with oxalyl chloride under the same conditions is mainly a benzocoumarandione:



This is the lactone of (hydroxynaphthyl)glyoxylic acid. It could have been formed by the saponification of the naphthol ether by aluminum chloride, and condensation of the naphthol with oxalyl chloride, followed by ring closure. As a matter of fact, it has been shown that β-naphthol with oxalyl chloride and aluminum chloride gives the foregoing lactone.[684]

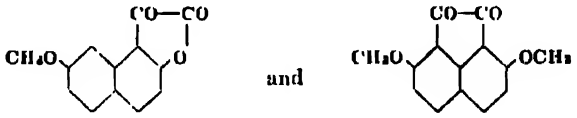
There is also formed in the condensation of oxalyl chloride with the β-naphthyl methyl ether, a small amount of methoxyacenaphthenequinone:



It has been shown by Liebermann and co-workers [685] that these types of substitution are to be expected with reactive compounds.

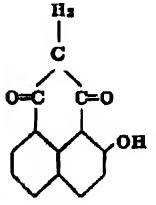
Reaction with β-ethoxy- naphthalene and oxalyl chloride proceeds as with the β-methoxy- compound.

The reaction with 2,7-dimethoxynaphthalene also results in the formation of a lactone and an acenaphthenequinone derivative:



β-Naphthyl benzyl ether with oxalyl chloride yields neither lactone nor acenaphthaquinone; instead the product contained a new yellow acid which has not been investigated.[682] The reaction was also studied with β-naphthyl phenyl ether, and with 2,7-dimethoxynaphthalene.

Malonyl chloride and β-naphthyl methyl ether in the presence of aluminum chloride in nitrobenzene is reported to give an indandione of the type:



[684] M. Giua and V. de Francesis, *Gazz. chim. ital.*, 54, 509-516 (1924); *J. Chem. Soc. Abs.*, 126 (I), 1092 (1924).
[685] C. Liebermann and co-workers, *Ber.*, 45, 1186-1217 (1912).

Here demethylation of the methoxy- group in the *ortho*- position to the carbonyl occurs.[686]

The reaction of α-naphthyl methyl ether with benzoyl chloride and aluminum chloride in carbon disulfide was studied by Fierz-David and Jaccard,[687] who reported a 68 per cent yield of 4-benzoyl-1-methoxynaphthalene. Using nitrobenzene as solvent, a temperature of 0°, and a reaction time of eighteen hours, Fieser and Bradsher[688] obtained an 84 per cent yield of the ketone.

Upon condensing benzoyl chloride with β-naphthyl methyl ether by means of aluminum chloride in carbon disulfide, an 85 per cent yield of 1-benzoyl-2-methoxynaphthalene was secured.[689]

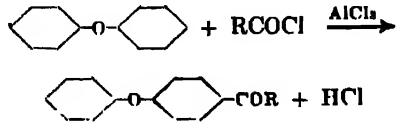
The reaction of cinnamoyl chloride with α-ethoxynaphthalene has been reported to give a ketone which crystallizes from alcohol in needles melting at 85-86°.[690]

An interesting condensation is that of α-naphthyl methyl ether and the chloride of 4-methylhydrindene-7-carboxylic acid with anhydrous aluminum chloride in tetrachloroethane to give 4-methyl-7-(4'-methoxy-1'-naphthoyl)-hydrindene in 82 per cent yield.[691]

Dimethoxynaphthalenes and benzoyl chloride have been reacted in the presence of aluminum chloride. 1,5-Dimethoxynaphthalene gives a 90 per cent yield of 1,5-dimethoxy-4,8-dibenzoylnaphthalene, m.p. 356-368°. Condensation of 2,6-dimethoxynaphthalene with benzoyl chloride and aluminum chloride in carbon disulfide gave 50 per cent of 2,6-dihydroxy-1,5-dibenzoylnaphthalene (m.p. 275°), a cleavage of the methoxy- groups occurring under the reaction conditions.[692] Although diacylation is unusual in Friedel-Crafts acylation, it is here facilitated by the presence of the two methoxy- groups.

A study of the by-products formed in the Friedel-Crafts synthesis of ketones from acid chlorides and naphthol ethers has been made.[693]

Diphenyl Ethers



Diphenyl ether was reacted with acetyl chloride by Kipper.[694] Using 1 mole of the ether, 1½ moles of acetyl chloride and 1½ moles of aluminum chloride with carbon disulfide, there was obtained a 90 per cent yield of

[686] R. Black, H. Shaw, and T. K. Walker, *J. Chem. Soc.*, 272-279 (1931); *Brit. Chem. Abs.*-A, 467 (1931).
[687] H. E. Fierz-David and G. Jaccard, *Helv. Chim. Acta*, 11, 1042-1047 (1928); *C. A.*, 23, 832.
[688] L. F. Fieser and C. K. Bradsher, *J. Am. Chem. Soc.*, 61, 417-423 (1939).
[689] F. E. Ray and W. A. Moomaw, *J. Am. Chem. Soc.*, 55, 3838-3838 (1933).
[690] F. Stockhausen and L. Gattermann, *Ber.*, 25, 3535-3538 (1892); *J. Chem. Soc. Abs.*, 64 (I), 163 (1893).
[691] L. F. Fieser and V. Desreux, *J. Am. Chem. Soc.*, 60, 2255-2262 (1938).
[692] Hans E. Fierz-David and G. Jaccard, *Helv. Chim. Acta*, 11, 1042-1047 (1928).
[693] P. E. Popov, *J. Gen. Chem. (U. S. S. R.)*, 5, 986-992 (1935); *C. A.*, 30, 1049.
[694] H. Kipper, *Ber.*, 38, 3490-3498 (1905); *J. Chem. Soc. Abs.*, 88 (I), 648 (1905).

p-phenoxyacetophenone, $C_6H_5OC_6H_4.COCH_3$, b.p. 318-325° and m.p. 45°. Dilthey and co-workers[695] obtained a 60 per cent yield of the diacetyl derivative, 4,4'-diacetyldiphenyl ether, m.p. 100-101°. Since under certain conditions aluminum chloride causes the hydrolysis of the methoxy-group, in the reaction of acetyl chloride with *p*-methoxydiphenyl ether Tomita[696] obtained the hydroxy- ketone, 4-hydroxy-3,4'-diacetyldiphenyl ether, m. 120°. Tomita used 10 g of the ether, 12 g of the chloride in 15 cc of carbon disulfide and 20 g of aluminum chloride.

The reaction of chloroacetyl chloride with diphenyl ether is described by Kunckell[697] who obtained bis-(ω-chloroacetylphenyl) ether, melting at 111°. Tomita[698] reports that the product of the reaction is 4,4'-bis-(ω-chloroacetylphenyl) ether, m.p. 102-104°.

This compound is also described in a patent to Schering-Kahlbaum, A.-G.,[699] which claims the condensation of diphenyl ether with halogenoacetyl chlorides in the presence of aluminum chloride. Using 10 parts of diphenyl ether and 10 parts of chloroacetyl chloride with 23 parts of aluminum chloride, there was obtained the disubstituted ether, 4,4'-bis-(ω-chloroacetylphenyl) ether, m.p. 102°. The corresponding bromo-derivative, 4,4'-bis-(ω-bromoacetylphenyl) ether (m.p. 121°) was similarly prepared. The reaction of chloroacetyl chloride with diphenyl ether is further described by von Schickh.[700] Here, with cooling and stirring, a mixture of 19 g of the ether and 19 g of the acetyl chloride was gradually added to 23 g of sublimed aluminum chloride. The yield of the diacylated ether (m.p. 102°) was 43 per cent of theoretical.

In the Schering-Kahlbaum patent, it had been assumed that as long as the 4,4'-positions were not occupied, the Friedel-Crafts reaction would give *p,p'*-derivatives. There was thus claimed the formation 4-ω-chloroacetylphenyl 2-methoxy-4-ω-chloroacetylphenyl ether from 2-methoxyphenyl phenyl ether and chloroacetyl chloride. Similarly, from bis-(2-methoxyphenyl) ether and the chloride, there was claimed the formation of bis-(2-methoxy-4-ω-chloroacetylphenyl) ether. Tomita[701] re-examined the reaction and showed that the acetyl or chloroacetyl group does not enter the 4,4'- positions, but enters the 4',5- or the 5,5'- positions He reported the formation of 5-acetyl-2-methoxyphenyl 4-acetylphenyl ether (m.p. 142°) from 2-methoxyphenyl phenyl ether and 2 moles of acetyl chloride in the presence of aluminum chloride. In the same way he prepared 5-ω-chloroacetyl-2-methoxyphenyl 4-ω-chloroacetylphenyl ether (m.p. 148°) using chloroacetyl chloride and the same ether. With 10 g of 4-methoxyphenyl phenyl ether and 17 g of chloroacetyl chloride in 15 cc of carbon disulfide with 20 g of aluminum chloride, Tomita[702] secured 4-hydroxy-3-ω-chloroacetylphenyl 3-ω-chloroacetylphenyl ether,

[695] W. Dilthey, E. Bach, H. Grütering and E. Hausdorfer, *J. prakt. Chem.*, 117, 337-368 (1927) *C. A.*, 22, 769.
[696] M. Tomita, *J. pharm. Soc. Japan*, 57, 689-695 (1937); *C. A.*, 32, 128.
[697] F. Kunckell, *Ber deut Pharm. Ges.*, 23, 188-227 (1890); *C. Z.*, 1913, I, 1769.
[698] M. Tomita, *J. pharm Soc Japan*, 56, 906-912 (1936), *C. A.*, 31, 3484
[699] U. S. P. 1,717,424; Brit. P. 286,688 (1928); German P. 492,321 (1927) to Otto von Schickh (to Schering-Kahlbaum A.-G.); *C. Z.*, 1929, II, 1430.
[700] O. von Schickh, *Ber.*, 69, 242-244 (1936); *C. A.*, 30, 8186.
[701] M. Tomita, *J. pharm. Soc. Japan*, 54, 897-904 (1934); *C. A.*, 30, 8185.
[702] M. Tomita, *J. pharm. Soc. Japan*, 57, 689-695 (1937); *C. A.*, 32, 128.

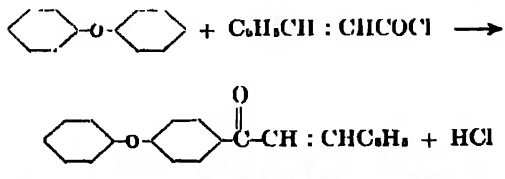
m.p. 155°. Here a hydrolysis of the methoxy- group had occurred. From bis-(2-methoxyphenyl) ether and chloroacetyl chloride he secured bis-(5-ω-chloroacetyl-2-methoxyphenyl) ether, m.p. 154-155°.[703] von Schickh [700] thereupon repeated the work and stated, as Tomita had found, that in the case of substituted diphenyl ethers, acylation does not necessarily result in the formation of *p,p'*- derivatives.

In order to study further the orientation of acyl groups in the Friedel-Crafts reaction with alkoxy-substituted diphenyl ethers, Tomita [704] reacted some *o*-alkoxydiphenyl ethers with acetyl chloride. With 3 g of 2-propoxyphenyl phenyl ether and 3.5 g of the chloride in 10 cc of carbon disulfide and 6 g of aluminum chloride he obtained 2-propoxy-5-acetylphenyl 4-acetylphenyl ether, m.p. 99°. Using the same proportion of reactants he secured from isoamoxyphenyl phenyl ether the correspondingly substituted derivative, 2-isoamoxy-5-acetylphenyl 4-acetylphenyl ether, m.p. 56-59°. Later, Tomita,[705] reacted 2.3 g of bis-(4-methoxyphenyl) ether with 2.5 g of acetyl chloride in the presence of 4 g of aluminum chloride and obtained a 1.2 g yield of bis-(3-acetyl-4-methoxyphenyl) ether, m.p. 133°. He thus showed that the position occupied by the alkoxy- substituent influences the orientation of the entering acyl group.

Diphenyl ethers, or substituted diphenyl ethers, have been condensed with higher fatty acid chlorides, such as stearoyl chloride, myristyl chloride, lauroyl chloride, caproyl chloride. The resulting products are of waxy character which find application in electrical insulation and as waxing and polishing compositions.[706]

Benzoyl chloride was reacted with diphenyl ether by Kipper.[707] He added a mixture of 1 mole of the chloride and 1 mole of the ether to 2½ moles of aluminum chloride in carbon disulfide and secured a 97 per cent yield of 4-benzoylphenyl phenyl ether, $C_6H_5OC_6H_4COC_6H_5$, m.p. 71°. Using 15 g of the ether and 20 g of the chloride with 50-61 g of aluminum chloride in carbon disulfide, Dilthey and co-workers [708] reported a 90 per cent yield of bis-(4-benzoylphenyl) ether, m.p. 163-164°.

The Friedel-Crafts reaction of cinnamoyl chloride with diphenyl ether takes place very slowly even in direct sunlight, but the yield is good. Benzal-*p*-phenoxyacetophenone (m.p. 85°) is formed [709]:

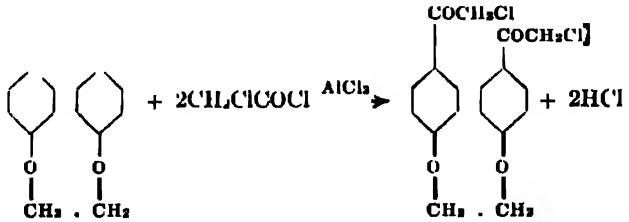


[703] M. Tomita, *J. pharm. Soc. Japan*, 54, 897-904 (1934); *C. A.*, 30, 8185.
[704] M. Tomita, *J. pharm. Soc. Japan*, 56, 492-497 (1936); *C. A.*, 30, 8186; *C. Z.*, 1936, II, 3673.
[705] M. Tomita, *J. pharm. Soc. Japan*, 57, 689-695 (1937); *C. A.*, 32, 128.
[706] U. S. P. 2,033,540 (1936) to A. W. Ralston and C. W. Christensen (to Armour and Company); U. S. P. 2,189,283 (1940) to A. W. Ralston and R. J. Vander Wal (to Armour and Company).
[707] H. Kipper, *Ber.*, 38, 2490-2493 (1905); *J. Chem. Soc. Abs.*, 88 (I), 648 (1905).
[708] W. Dilthey, E. Bach, H. Grütering, and E. Hausdorfer, *J. prakt. Chem.*, 117, 337-365 (1927); *C. A.*, 22, 709.
[709] E. P. Kohler, G. L. Heritage, and M. C. Burnley, *Am. Chem. J.*, 44, 60-76 (1910); *C. A.*, 4, 2637.

Blicke and Weinkauff[710] obtained 4-methoxy-4'-benzoylbiphenyl (m.p. 168-169°) by allowing 9 g of 4-methoxybiphenyl, 7 g of benzoyl chloride, 8 g of aluminum chloride, and 40 cc of carbon disulfide to remain at ordinary temperature for 24 hours. This preparation was repeated by Hey and Jackson.[711] Using the same quantities of materials and the same reaction period, these workers obtained 4-methoxy-4'-benzoylbiphenyl (m.p. 166°) and another substance (m.p. 170°) which they regarded as 4-methoxy-3,4'-dibenzoylbiphenyl.

4-Methoxy-4'-methylbiphenyl has been reacted with oxalyl chloride and aluminum chloride in carbon disulfide at 0° to give 4-hydroxy-3,3'-dicarboxy-4'-methylbiphenyl, m.p. 280°.[712] Here, as in the case of aromatic compounds in which the phenyl radicals are joined through an aliphatic linkage, oxalyl chloride acts as carboxylating agent.[713] Cleavage of the methoxy- group occurred during reaction.

Ethylene glycol diphenyl ether and chloroacetyl chloride yields ethylene glycol bis-(4-chloroacetylphenyl ether) (m.p. 160-165°) according to [714]:



Phenanthryl Ethers

4-Methoxyphenanthrene has been found to react easily with acetyl and propionyl chlorides in the presence of aluminum chloride to give 4-methoxy-(?)-acetylphenanthrene (m.p. 122.5-123.5°) and 4-methoxy-(?)-propionylphenanthrene (m.p. 116°) in 70 per cent yields.[715] Analogous reaction with 1-methoxyphenanthrene, using nitrobenzene or *sym*-tetrachloroethane, or a mixture of both, as solvents, could not be effected

The methyl ether of 2-hydroxy-9,10-dihydrophenanthrene has been reacted with acetyl chloride by the Friedel-Crafts reaction, but the acetyl derivatives have not been identified.[716]

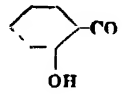
Reaction of Ethers with Nitrogenous Acid Chlorides

Nitroaroyl Chlorides

p-Nitrobenzoyl chlorides undergo normal Friedel-Crafts reactions with anisole, phenetole, and *p*-tolyl methyl ether.

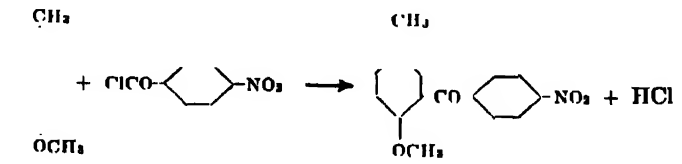
[710] F. F. Blicke and O. J. Weinkauff, *J. Am. Chem. Soc.*, 54, 330-334 (1932).
[711] D. H. Hey and E. R. B. Jackson, *J. Chem. Soc.*, 1936, 802-806.
[712] N. Chatterjee, *J. Indian Chem. Soc.*, 12, 690-692 (1935); *Brit. Chem. Abs.*-A, 728 (1936).
[713] C. Liebermann and co-workers, *Ber.*, 45, 1186-1217 (1912); *J. Chem. Soc. Abs.*, 102 (I), 464
[714] F. Kunckell and F. Johannsen, *Ber.*, 31, 169-172 (1898).
[715] H. M. Duvall and E. Mosettig, *J. Am. Chem. Soc.*, 60, 2408-2413 (1938).
[716] E. Mosettig and A. H. Stuart, *J. Am. Chem. Soc.*, 61, 1-7 (1939).

Condensation of *p*-nitrobenzoyl chloride with anisole in carbon disulfide solution by means of aluminum chloride gives 4-methoxy-4′-nitrobenzophenone as the principal product. With phenetole, under similar conditions, 4-ethoxy-4′-nitrobenzophenone was also obtained; but 2-hydroxy-4′-nitrobenzophenone is also formed, together with traces of 4-hydroxy-4′-nitrobenzophenone.[717] The production of the latter compound, of course, can be explained by hydrolysis of the methoxy- group in the principal product, but the formation of large amounts of 2-hydroxy-4′-nitrobenzophenone,



was unusual. Obviously, during the acylation, 2-ethoxy-4′-nitrobenzophenone had been formed, together with the 4-ethoxy- isomer. The fact that a greater amount of 2-hydroxy-4′-nitrobenzophenone was formed than of the 4-hydroxy-4′-nitro ketone is due to the fact that an *ortho*-methoxy- group is saponified more readily than is the *para*- group.[718]

The easy cleavage of the *o*-methoxy- is also shown in the condensation of *p*-cresol methyl ether with *p*-nitrobenzoyl chloride:

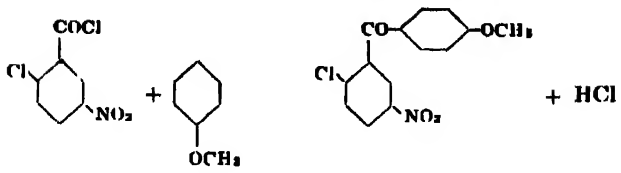


2-Methoxy-4′-nitro-5-methylbenzophenone (m.p. 101-102°) was formed, but there was also formed its hydrolysis product, 2-hydroxy-4′-nitro-5-methylbenzophenone, m.p. 142-143°.

A *meta*-nitro-substituted benzoyl chloride may likewise be used in Friedel-Crafts acylation of phenol ethers. Thus phenetole, 3-nitrobenzoyl chloride and aluminum chloride in carbon disulfide give 3-nitro-4′-ethoxybenzophenone (m.p. 79-81°) which upon further treatment with aluminum chloride is converted to the corresponding hydroxy- compound, 3-nitro-4′-hydroxybenzophenone.[719]

Upon dissolving 3-nitro-6-chlorobenzoic acid together with phosphorus pentachloride in carbon disulfide and subsequent addition of anisole and aluminum chloride, a normal condensation occurs [720]:

[717] K. v. Auwers, *Ber.*, 36, 3902-3902 (1903); *J. Chem. Soc. Abs.*, 1904 (I), 67.
[718] K. v. Auwers and E. Rietz, *Ber.*, 40, 3514-3521 (1907); *J. Chem. Soc. Abs.*, 92 (I), 988 (1907).
[719] K. v. Auwers, *Ber.*, 36, 3890-3892 (1903).
[720] F. Ullmann and H. W. Ernst, *Ber.*, 39, 307 (1906).



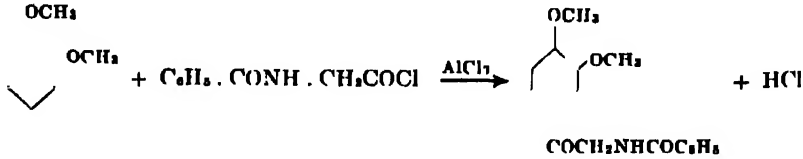
The 3-nitro-6-chloro-4'-methoxybenzophenone melts at 105°.

Although Friedel-Crafts acylation of aromatic hydrocarbons does not usually take place with *o*-nitro aroyl chlorides, the reaction of *o*-nitro benzoyl chloride with anisole and aluminum chloride in carbon disulfide with cooling has been reported to give 2-nitro-4'-methoxybenzophenone.[721]

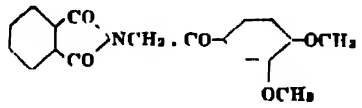
Amido- and Imido- Acid Chlorides

As with aromatic hydrocarbons, various amido- and imido- acid chlorides have been reacted with phenol ethers and aluminum chloride.

Benzamidoacetyl chloride (hippuryl chloride) condenses with veratrole, or other 1,2-dialkoxy- benzenes, in the presence of aluminum chloride to give compounds in which the hippuryl group is substituted in the *para*- position to one of the alkoxy- groups.[722] Veratrole, for example, gives 4-benzamidoacetylveratrole (m.p. 155°) according to the scheme.



Upon heating phthalylglycyl chloride with veratrole in the presence of aluminum chloride, α-phthalimido-3,4-dimethoxyacetophenone is obtained [723]:



Condensation of α- and β-phthalimido-propionic acid chlorides with veratrole takes place in like manner.

Böttcher [724] has investigated the condensation of other phthalimido acid chlorides with anisole, veratrole, and dimethoxybenzenes.

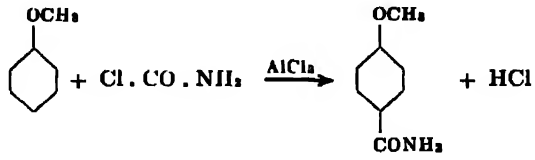
The decomposition of oxalyl chloride by aluminum chloride into carbon monoxide and phosgene makes it very difficult to prepare *ortho*-diketones by its use in the Friedel-Crafts reaction. Staudinger and co-workers [725] tried to overcome this difficulty by replacing oxalyl chlo-

[721] K. v. Auwers, *Ber.*, 36, 3890-3902 (1903).
[722] German P. 185,598 to Farbenfabriken vorm. Friedr. Bayer and Co.; *J. Chem. Soc. Abs.*, 92, I 1049 (1907).
[723] German P. 209,902 to Bayer and Co.; *C. Z.*, 1909, I, 1951.
[724] K. A. Böttcher, *Ber.*, 46, 3155-3167 (1913).
[725] H. Staudinger, H. Goldstein, and E. Schlenker, *Helv. Chim. Acta*, 4, 343-364 (1921); *C. A.*, 15, 3446.

ride with imido chloride derivatives of oxalic acid. With the methyl and ethyl ethers of 2-naphthol they secured 75 and 44 per cent yields, respectively, of the corresponding acenaphthene quinones.

Carbamyl Chlorides and Phenol Ethers

According to Gattermann,[726] phenol ethers react readily with carbamyl chloride in the presence of aluminum chloride to give the corresponding acid amides, the reaction with anisole proceeding:

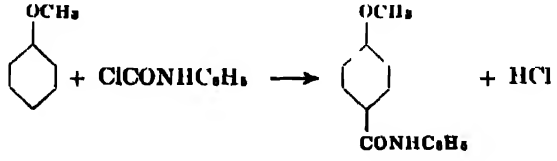


The reaction is a general one for mono- or polyphenol ethers. Gattermann gradually added an amount of powdered aluminum chloride equivalent to the amount of carbamyl chloride used to a mixture consisting of 1 molecular weight of the phenol ether and 1½ molecular weights of carbamyl chloride in carbon disulfide. If reaction did not occur immediately, short heating on a water-bath was sufficient to initiate it. Acid amides were prepared from the following ethers:

phenetole
o-cresol methyl ether
o-cresol ethyl ether
p-cresol methyl ether
p-cresol ethyl ether
thymol methyl ether
thymol ethyl ether

Substitution occurred preferably *para*- to the alkoxy- group, or *ortho*- to it, if the *p*- position was not available.

In 1885 Leuckart and Schmidt [727] reported that phenyl isocyanate in the presence of aluminum chloride reacted with phenol ethers to yield anilides, the reaction probably occurring through intermediate formation of phenylcarbamyl chloride and subsequent reaction of the acid halide with the ether:



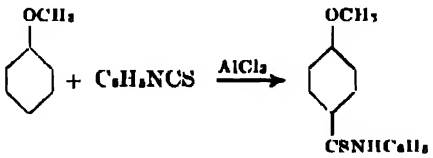
A similar reaction occurred with phenetole. Small quantities of aromatic hydroxy- acids were also formed during the condensation, indicating cleavage of the methoxy- group and hydrolysis of the amide. *p*-Tolyl

[726] L. Gattermann, *Ann.*, 244, 61-76 (1888).
[727] R. Leuckart and M. Schmidt, *Ber.*, 18, 2335-2341 (1885); *J. Chem. Soc. Abs.*, 48, 1234 (1885).

isocyanate and naphthyl isocyanate reacted in a manner similar to phenyl isocyanate. Gattermann's work on carbamyl chloride with phenol ethers was an outgrowth of this study.

Reactants that yield carbamyl chloride may be used for the production of amides of phenol ethers. Thus, anisole with cyanic acid and hydrogen chloride in the presence of aluminum chloride gives anisamide, m.p. 162-163°. Phenetole likewise gives the amide of ethoxybenzoic acid, m.p. 201°. Both reactions take place readily, giving good yields of the amides.[728]

Aryl isothiocyanates condense with phenolic ethers in the presence of aluminum chloride to give thioanilides. Thus phenyl isothiocyanate (which probably is changed to the unstable phenylthiocarbamyl chloride during the reaction) reacts with anisole and aluminum chloride to give 4-methoxythiobenzanilide, according to the reaction:



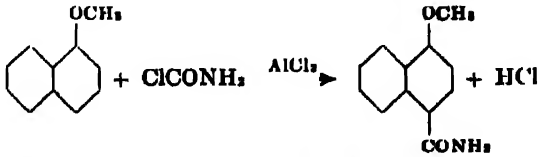
In the same way, Tust and Gattermann [729] prepared the thioanilide of phenetole.

Chloroanisole and chlorophenetole undergo like reaction.[730] The reaction appears to be general for aryl isothiocyanates, for *o*- and *p*-tolyl isothiocyanate and *m*-xylyl thiocyanate have been shown to undergo analogous reaction with anisole and phenetole.

Reaction of alkylated phenol ethers, or of polyhydric phenol ethers is likewise effected. Thus thymol methyl ether and phenyl isothiocyanate with aluminum chloride give 2-methyl-4-methoxy-5-isopropyl thiobenzanilide; resorcinol diethyl ether similarly yields 2,4-diethoxythiobenzanilide.[730]

Carbamyl Chloride and Ethers of Polynuclear Phenols

Carbamyl chloride in the presence of aluminum chloride undergoes a Friedel-Crafts reaction with naphthol ethers to give amides. According to Gattermann,[731] the reaction proceeds readily, for example with α-naphthyl methyl ether according to the equation:



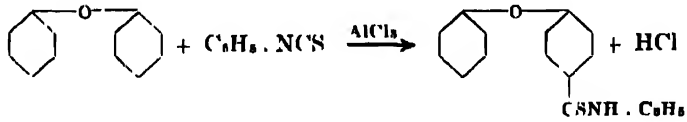
[728] L. Gattermann und A. Rossolymo, *Ber.*, 23, 1190-1199 (1890); *J. Chem. Soc. Abs.*, 58 (II), 974-975 (1890).
[729] K. Tust and L. Gattermann, *Ber.*, 25 3528-3530 (1892).
[730] L. Gattermann, *J. prakt. Chem.*, 59 (II), 572-594 (1899); *J. Chem. Soc. Abs.*, 76 (I), 694 (1899)
[731] L. Gattermann, *Ann.*, 244, 71-76 (1888).

Reaction with α-naphthyl ethyl ether is analogous. With methyl- or ethyl-β-naphthyl ethers, amides were obtained, melting at 186° and 161°, respectively. Their structure was not established.

An amide of α-naphthyl ethyl ether may also be prepared by treating the ether with cyanic acid and hydrogen chloride in the presence of aluminum chloride.[732]

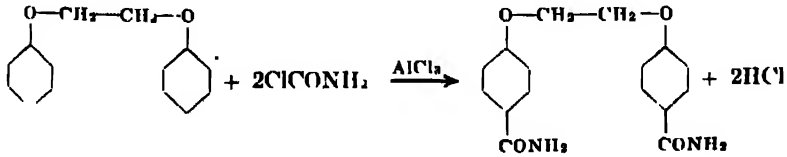
Phenyl isothiocyanate in the presence of aluminum chloride reacts with α-naphthyl ethyl ether to give a thioanilide, $C_6H_5NH.CS.C_{10}H_6.OC_2H_5$, m.p. 199-200°. The reaction probably occurs through intermediate formation of phenylthiocarbamyl chloride.[733]

Aryl isothiocyanates, which under the influence of aluminum chloride act as the corresponding thiocarbamyl chlorides, react with diphenyl ether to give the corresponding thioanilides. Thus diphenyl ether with phenyl isothiocyanate gives *p*-phenoxythiobenzanilide (m.p. 133°) probably according to the reaction:



Similarly with ethylene glycol diphenyl ether, a thioanilide of the formula $C_2H_4(O.C_6H_4.CS.NHC_6H_5)_2$ is obtained.[734]

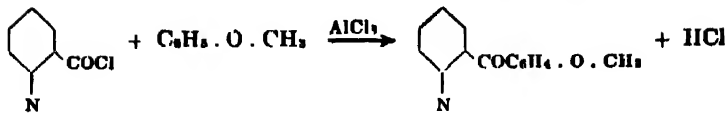
According to Gattermann,[735] if carbamyl chloride is reacted with diphenyl in the presence of aluminum chloride, only mono-substitution of the $CONH_2$ group occurs. However, with ethylene glycol diphenyl ether, di-substitution occurs, the reaction proceeding:



Heterocyclic Acid Chlorides

Because pyridine does not undergo Friedel-Crafts acylation, pyridyl ketones are prepared by reaction of pyridine acid chlorides with the hydrocarbon or ether. For example, reaction of picolinic acid chloride with anisole and aluminum chloride gives α-pyridyl anisyl ketone[736]:

[732] L. Gattermann and A. Rossolymo, *Ber.*, 23, 1190-1199 (1890); *J. Chem. Soc. Abs.*, 58 (II), 974-975 (1890).
[733] K. Tust and L. Gattermann, *Ber.*, 25, 3528-3530 (1892).
[734] L. Gattermann, *J. prakt. Chem.*, 59 (II), 572-594 (1899); *J. Chem. Soc. Abs.*, 76 (I), 694 (1899)
[735] L. Gattermann, *Ann.*, 244, 69-70 (1888).
[736] R. Wolffenstein and F. Hartwich, *Ber.*, 48, 3048-3049 (1915); *C. A.*, 10, 788.



Like condensation occurs with nicotinic acid chloride.

Phenol Ethers and Sulfur-containing Acyl Halides

The reaction of thionyl chloride with phenol ethers in the presence of aluminum chloride with production of thio-ethers was described in 1894 by Loth and Michaelis.[747] These workers prepared thioanisole from anisole. Tetrabromothioanisole and thiophenetole were also prepared from the corresponding ethers. These compounds were described as having the compositions:

$$S(C_6H_4OCH_3)_2$$
$$S(C_6H_2Br_2OCH_3)_2$$
$$S(C_6H_4OC_2H_5)_2$$

These investigators added aluminum chloride to an approximately equimolecular mixture of the ether and thionyl chloride, and when the violent reaction was over they diluted the mixture with dry ether. The solution was then warmed on a water-bath to complete the reaction. Since sulfoxides are reduced to sulfides by warming with thionyl chloride, the primary reaction products may well have been sulfoxides:

$$2C_6H_5OCH_3 + SOCl_2 \xrightarrow{AlCl_3} CH_3 . OC_6H_4 . SO . C_6H_4 . O . CH_3 + 2HCl$$

As a matter of fact Smiles and Le Rossignol [748] have shown that sulfoxides are the primary reaction products of ethers and thionyl chloride in the presence of aluminum chloride. These workers also prepared aromatic sulfonium bases by reacting phenol ethers with thionyl chloride, and then reacting the primarily formed sulfoxide with an additional molecule of phenol ether. With phenetole, for example, the reaction for the production of triphenetyl sulfonium chloride is:

$$\text{(I)}\quad 2C_6H_5 . O . C_2H_5 + SOCl_2 \xrightarrow{AlCl_3} 2HCl + SO(C_6H_4 . O . C_2H_5)_2$$

$$\text{(II)}\quad SO(C_6H_4 . O . C_2H_5)_2 + HCl \longrightarrow (C_6H_4 . O . C_2H_5)_2SCl . OH$$

$$\text{(III)}\quad (C_6H_4 . O . C_2H_5)_2SCl . OH + C_6H_4 . O . C_2H_5 + SOCl_2 \xrightarrow{AlCl_3} SO_2 + 2HCl + (C_6H_4 . O . C_2H_5)_3SCl$$

Thus a mixture of phenetole and thionylchloride in the proportion of 3 molecules of the former to 2 molecules of the latter yields, on treatment with aluminum chloride, almost exclusively the sulfonium chloride in practically theoretical yield.

[747] F. Loth and A. Michaelis, *Ber.*, **27**, 2540-48 (1894).
[748] S. Smiles and R. Le Rossignol, *J. Chem. Soc.*, **89**, 696-708 (1906).

The sulfoxide is obtained by avoiding any excess of condensing agent, and by using one molecular proportion of thionyl chloride with two proportions of phenetole. It could be obtained, however, only in a 40 per cent of theoretical yield.

The production of aromatic sulfinyl chloride postulated in the series of transformation resulting in the formation of the aromatic sulfonium chlorides was later proved by Hilditch and Smiles,[739] when they succeeded in preparing aromatic sulfinyl chlorides by the action of an excess of thionyl chloride on the sulfinic acids at ordinary temperatures.

Thiophosgene, $CSCl_2$, reacts with phenol ethers and aluminum chloride, in absence of solvents, to give corresponding thioketones.[740] The reaction with anisole, for example, proceeds:

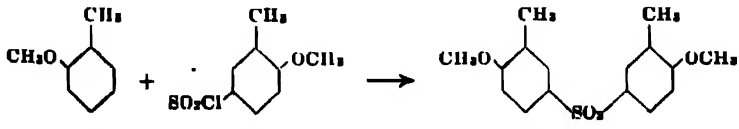
$$C_6H_5.O.CH_3 + CSCl_2 \xrightarrow{AlCl_3} CS(C_6H_4.O.CH_3)_2 + 2HCl$$

The thioketone (m.p. 115°) can easily be converted into *p,p'*-dimethoxybenzophenone.

Other phenol ethers which have been found to undergo the reaction are listed, together with the products obtained:

Phenol Ether	Thioketone	m.p. (°C).
Phenetole	$CS(C_6H_4.OC_2H_5)_2$	118–119
n-Propyl phenyl ether	$CS(C_6H_4.OC_3H_7)_2$	105–106
o-Cresol ethyl ether	$CS(C_6H_3CH_3.O.C_2H_5)_2$	117–118
o-Cresol methyl ether	?	114
o-Chloroanisole	$CS(C_6H_3Cl.OCH_3)_2$	178–179
o-Chlorophenetole	?	141–142
o-Bromoanisole	$CS(C_6H_3Br.OCH_3)_2$	189–190

Treatment of *o*-methoxytoluene with 2-methoxytoluene-5-sulfonyl chloride and aluminum chloride gives 6,6'-dimethoxy-di-*m*-tolyl sulfone.[741] This is a normal Friedel-Crafts condensation:



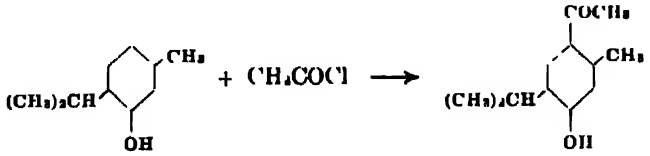
p-Tolyl methyl ether with *o*-carbethoxy-*p*-cresol-3-sulfonyl chloride in the presence of aluminum chloride has been shown by Heppenstall and Smiles[742] to give 2-hydroxy-2'-methoxy-5,5'-dimethyldiphenyl sulfone. Benzenesulfonyl chloride and *p*-tolyl methyl ether react analogously.[743]

Reactions of Acyl Chlorides with Phenols

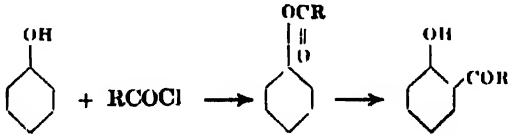
Early reports of aluminum chloride-catalyzed reactions stated that aluminum chloride could not be used as a condensing agent with phenolic

[739] T. P. Hilditch and S. Smiles, *Ber.*, 41, 4113-4116 (1908); *J. Chem. Soc. Abs.*, 96 (1) 18 (1909).
[740] L. Gattermann, *Ber.*, 28, 2863-2877 (1895).
[741] G. B. Kolhatkar and K. V. Bokil, *J. Indian Chem. Soc.*, 7, 843-850 (1930); *Brit. Chem. Abs.-A*, 412 (1931).
[742] M. E. Heppenstall and S. Smiles, *J. Chem. Soc.*, 899-905 (1938).
[743] J. H. Simons, S. Archer, and D. I. Randall, *J. Am. Chem. Soc.*, 62, 485-6 (1940).

compounds.[744] In 1897, however, a patent was issued to Behn [745] in which he claimed the production, in almost theoretical yield, of thymyl methyl ketone by the reaction of thymol with acetyl chloride. He used nitrobenzene as a solvent, claiming that its use was very advantageous in that it serves as a solvent for the catalyst complex resulting from the Friedel-Crafts synthesis. With 10 g of thymol, he used about 50 cc of nitrobenzene, and then added to this solution an excess of the calculated amount of acetyl chloride. Thirty g of aluminum chloride was added gradually. The reaction occurred according to the scheme:



The mechanism of Friedel-Crafts ketone syntheses with phenols has not been satisfactorily elucidated. It may take place through primary esterification and subsequent Fries rearrangement * to the hydroxyketone:



This theory is contradicted by several investigators, who believe that the Fries rearrangement is not a true rearrangement, but an intermolecular acylation, proceeding through primary hydrolysis of the ester, and subsequent introduction of the cleaved acyl group into the nucleus of the benzene ring.

The fact that aluminum chloride and phenols yield molecular compounds having the formula $ArO.AlCl_2$, which react with acyl halides to give hydroxy- ketones,† also weakens the theory involving primary esterification and subsequent Fries rearrangement in the Friedel-Crafts synthesis of hydroxy- ketones.

Rosenmund and Schulz [746] reported that the process claimed by Behn was suitable for the preparation of numerous ketones, and especially for the synthesis of monophenol ketones with long side chains. Less favorable results were obtained with polyphenols and with compounds in which the position *para-* to the hydroxyl was occupied.

The procedure of Rosenmund and Schulz was substantially that used

[744] C. Friedel and J. M. Crafts, *Compt. rend.*, **84**, 1453 (1877).
[745] German P. 95,901 (1897) to R. Behn; *C. Z.*, 1898, I, 1223.
* See Chapter 15.
† See page 354.
[746] K. W. Rosenmund and H. Schulz, *Arch. Pharmaz. Ber. deut. Pharm. Ges.*, 265, 808-819, (C. A. 1927, I, 3154.

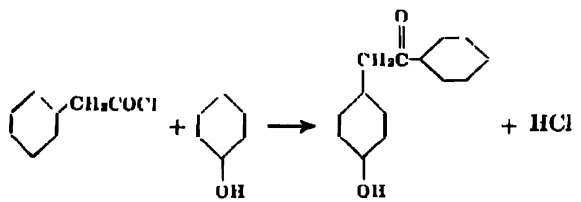
by Behn. To the solution of the phenol in 5 parts of dry nitrobenzene about 1 mole of the acid chloride was added, and then gradually, with cooling, the aluminum chloride (three times the amount of phenol used). The reaction mixture was allowed to stand overnight before isolation of the ketone. In this way the following compounds were prepared from the indicated phenols and acid chlorides:

Phenol	Acid Chloride	Ketone Obtained	m.p. (°C)
Thymol	acetyl	thymol methyl	125
Thymol	propionyl	thymol ethyl	112
Thymol	*n*-butyryl	thymol *n*-propyl	93
Thymol	isovaleryl	thymol isobutyl	108
Thymol	benzoyl	thymol phenyl	153
o-*n*-Propylphenol	acetyl	*o*-*n*-propylphenol methyl	87
o-*n*-Propylphenol	propionyl	*o*-*n*-propylphenol ethyl	80–81
o-*n*-Propylphenol	*n*-butyryl	*o*-*n*-propylphenol *n*-propyl	54
o-*n*-Propylphenol	isovaleryl	*o*-*n*-propylphenol isobutyl	b.p. 220/28 mm
o-*n*-Propylphenol	caprylic	*o*-*n*-propylphenol *n*-heptyl	60–61
Resorcinol	acetyl	resacetophenone	142
Pyrogallol	acetyl	gallacetophenone	167
Phloroglucinol	acetyl	phloracetophenone	218
Phloroglucinol	benzoyl	benzoylphloroglucinol	164–5
p-Cresol	acetyl	*o*-*o*-diacetyl-*p*-cresol	82

The reaction of *p*-cresol and acetyl chloride was effected as described above, except that 1.5 moles of acetyl chloride was used and the reaction mixture was heated for six days on a water-bath. Good yields were obtained in the reaction with resorcinol, but yields with pyrogallol were less. The method of preparation used here is not advantageous with phloroglucinol because this phenol is little soluble in nitrobenzene.

Using the same method, Rosenmund and Wha[747] prepared the 2-hydroxy-5-*p*-cymyl methyl ketone (m.p. 120°) from carvacrol and acetyl chloride. The corresponding ethyl ketone (m.p. 110°) and the propyl ketone (m.p. 90°) were also prepared.

By the action of aluminum chloride on phenylacetyl chloride and a phenol dissolved in nitrobenzene, various hydroxy- derivatives of desoxybenzoin, $C_6H_5CO.CH_2.C_6H_4$, have been prepared. Phenol thus yields *p*-hydroxydesoxybenzoin[748]:

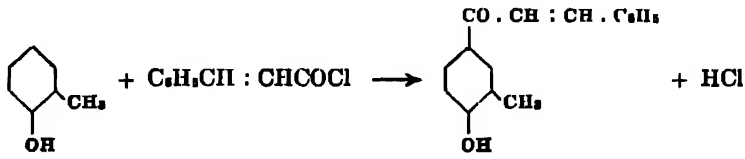


A similar reaction occurs with *o*- or with *m*-cresol, yielding 4-hydroxy-3-methyldesoxybenzoin or 4-hydroxy-2-methyldesoxybenzoin.[749] The three dihydroxy- benzenes—resorcinol, pyrocatechol, and hydroquinone

[747] K. W. Rosenmund and C. Wha, *Arch. Pharm.*, 266, 407-411 (1928).
[748] S. Weisl, *Monatsh.*, 26, 977-1002 (1905); *J. Chem. Soc. Abs.*, 88, I, 904-905 (1905).
[749] E. Blau, *Monatsh.*, 26, 1149-1164 (1905); *J. Chem. Soc. Abs.*, 88, I, 905-906 (1905).

—react in like manner to give the corresponding dihydroxyphenylbenzoins.[750]

Heating *o*-cresol with cinnamoyl chloride and aluminum chloride in an excess of nitrobenzene yields (4-hydroxy-3-methylphenyl) styryl ketone (m.p. 137°) according to the reaction [751]:



Rosenmund and Schulz [746] advocated the solution of a phenol in 5 parts of nitrobenzene, subsequent addition of acyl halide, and then treatment with aluminum chloride. By slightly varying this process, John and Beetz [752] secured a 20-23 per cent yield of 6-ω-chloroacetylthymol. They dissolved thymol in 5 parts of nitrobenzene, and then added a solution of aluminum chloride in the chloroacetyl chloride.

Carvacrol with propionyl, butyryl, or isovaleryl chlorides under similar conditions, however, gives 70-90 per cent yields of the corresponding 5-acyl-2-hydroxy-1-methyl-4-isopropylbenzenes.[753] The reaction with acetyl chloride gives lower yields.[754]

In the Rosenmund process it is necessary that low temperatures be used. Sandulesco and Girard [755] reported that this need of cooling limits the method to the preparation of only small amounts of ketones. Another disadvantage is the large amount of nitrobenzene required. Sandulesco describes an improved process which depends on the observation that 1 mole of a phenol unites with 1 mole of aluminum chloride, with evolution of hydrogen chloride, with the formation of a product probably having the formula $ArO.AlCl_2$. This compound is almost liquid at 100° and of a resin-like consistency at room temperature. At 120-140° it reacts with acid chlorides, in the absence of a solvent, to form normal Friedel-Crafts condensation products of mixtures of *o*- and *p*-hydroxyaryl ketones in yields of 80-90 per cent. In one operation, 1000 g or more of phenol may be treated. The two processes were contrasted in the reaction of heptoyl chloride with phenol. In the presence of nitrobenzene the yields were found to be lower and the operating difficulties greater; 33 per cent of *o*- and 46 per cent of *p*-hydroxyphenyl hexyl ketone was secured. In the absence of solvent, about 45-60 per cent of *o*- and 30-40 per cent of *p*-derivative are formed, together with a little *o*-*p*-disubstituted derivative. In a series of similar reactions, the authors found that the *o*- compounds are differentiated from their isomers by the

[750] F. Finzi, *Monatsh.*, 26, 1119-1135 (1905); *J. Chem. Soc. Abs.*, 88, I, 906-907 (1905).
[751] G. Neurath, *Monatsh.*, 27, 1145-1156 (1906).
[752] H. John and P. Beetz, *J. prakt. Chem.*, 140, 171-174 (1937); *C. A.*, 32, 120.
[753] H. John and P. Beetz, *J. prakt. Chem.*, 143, 342-6 (1935); *C. A.*, 29, 7956.
[754] H. John and P. Beetz, *J. prakt. Chem.*, 137, 351-364 (1933); *C. A.*, 27, 4234.
[755] G. Sandulesco and A. Girard, *Bull. soc. chim.*, 47 (iv), 1300-1314 (1930); *Brit. Chem. Abs.* A, 234 (1931); *C. Z.*, 1931, I, 931. See also A. W. Ralston and S. T. Bauer, *J. of Org. Chem.*, 5, 165-70 (1940) for Friedel-Crafts acylation of phenol with caprylyl, lauroyl, palmitoyl, and stearoyl chlorides

solubility of the former in ethyl alcohol, insolubility in alkali, and lower melting and boiling points. The following ketones were prepared according to the new process, the *o*- and *p*- isomers both being secured in the reaction of phenol with the corresponding *n*-acyl chloride:

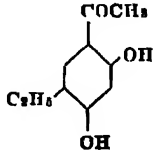
Ketone	b.p. (°C)	m. p. (°C)	yield (%)
o-Butyrylphenol	b_9 119	10.5–10.6	45
p-Butyrylphenol	b_9 187–188	107–107.5	
o-Valerylphenol	b_{10} 130	..	
p-Valerylphenol	b_{10} 197.5–198.5	63	29
o-Caproylphenol	b_{10} 142.3	17.2–17.4	56
p-Caproylphenol	b_{10} 207–208	61	34
o-Heptoylphenol	b_{10} 155–156	9.8	48
p-Heptoylphenol	b_9 214	91–91.5	41
o-Octoylphenol	b_{11} 169–170	22.3	45
p-Octoylphenol	b_{10} 224–225	62	38
o-Nonoylphenol	b_{10} 180	18.4	55
p-Nonoylphenol	b_{10} 232	54.5	35

Recently, Norris and Sturgis [756] prepared the molecular compound $C_6H_5O.AlCl_2$ from phenol and aluminum chloride and reacted it with acetyl chloride in the absence of a solvent. The products of the reaction when 19.2 g of phenol was used were:

o-hydroxyacetophenone	13.3 g
p-hydroxyacetophenone	5.1 g
phenacetein	4.0 g

The proportion of *ortho*- and *para*- isomers is in accordance with the findings of Sandulesco and Girard,[755] who secured 45-60 per cent of the *ortho*- and 30-40 per cent of the *para*-acyl phenols with the complex $C_6H_5O.AlCl_2$, also in the absence of solvents. The phenacetein produced is 2-(4′)-hydroxyphenyl-4-anhydromethyl-(1,4-benzopyranol), which has been shown [757] to be a condensation product of the *o*- with the *p*-hydroxyacetophenone.

The action of resorcinol and its derivatives with acetyl chloride has been investigated by Desai and Ekhlas.[758] Resorcinol treated with acetyl chloride and aluminum chloride in nitrobenzene gives only 2,4-dihydroxyacetophenone. 4-Ethylresorcinol similarly gives only 2,4-dihydroxy-5-ethylacetophenone:



In both cases, substitution does not occur between the two hydroxy-groups. With 5-methylresorcinol, however, two products are obtained.

[756] J. F. Norris and B. M. Sturgis, *J. Am. Chem. Soc.*, **61**, 1413-1417 (1939).
[757] C. Bulow, *Ber.*, **36**, 730-736 (1903).
[758] R. D. Desai and M. Ekhlas, *Proc. Indian Acad. Sci.* **9A**, 194-201 (1938); *C. A.*, **33**, 2119.

One is 4,7-dimethyl-5-hydroxycoumarin (m.p. 258°) and the other is orsacetophenone, m.p. 159-160°. The coumarin was formed by way of 5-methyl-2-acetyl-1,3-dihydroxybenzene. In this case substitution occurs between the two hydroxy- groups of resorcinol.

Rosenmund and Lohfert [759] prepared acyl derivatives of pyrocatechol, hydroquinone, and phloroglucinol by first dissolving the phenol and aluminum chloride in nitrobenzene and heating on a water-bath until hydrogen chloride ceased to be evolved. The acyl chloride was then added. The preparations are listed:

Phenol	Acid Chloride	Product	Yield (%)
Pyrocatechol	butyryl	butyropyrocatechol	27
Hydroquinone	acetyl	acetylhydroquinone	40
Hydroquinone	propionyl	propionylhydroquinone	40
Phloroglucinol	butyryl	butyrylphloroglucinol	
Phloroglucinol	capronyl	capronylphloroglucinol	63
Phloroglucinol	isovaleryl	isovalerylphloroglucinol	

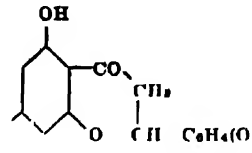
By the same method, the following aroyl derivatives were also prepared by Rosenmund and Rosenmund [760] from phloroglucinol and the indicated acid chlorides:

Aroyl Chloride	Product	m.p. (°C.)
Benzoyl	benzoylphloroglucinol	165
Phenylacetyl	phenylacetophloroglucinol	164–166
Anisoyl	anisoylphloroglucinol	177–178
(*p*-Carbethoxyoxy)-benzoyl	1-(4-carbethoxyoxy)-2,4,6-trihydroxybenzene	172

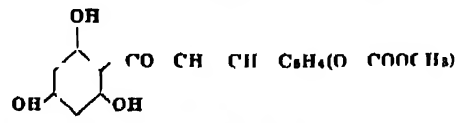
Cinnamoyl chloride with phloroglucinol yielded two unidentified compounds: A, having the empirical formula $C_{15}H_{12}O_4$ and melting at 202°, and the other melting at 210°. Shinoda and Sato,[761] who also worked on this reaction, secured, together with two other products, 5,7-dihydroxyflavanone (m.p. 203-204°), but they obtained no compound melting at 210°.

Rosenmund and Rosenmund [760] also reacted *p*-carbomethoxyoxycoumarylyl chloride with phloroglucinol, securing a flavanone (A) (m.p. 183-184°) and a chalcone (B) (m.p. 160°) of the following compositions:

(A)



(B)

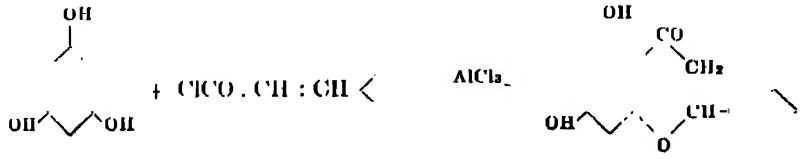


[759] K. W. Rosenmund and H. Lohfert, *Ber.*, 61, 2601-2607 (1928).
[760] K. W. Rosenmund and M. Rosenmund, *Ber.*, 61, 2606-2612 (1928).
[761] J. Shinoda and S. Sato, *J. Pharm. Soc. Japan*, 48 (558), 109-114, (560), 117-119, 119-120 (1) 8; *Brit. Chem. Abs.-A*, 139 (1928).

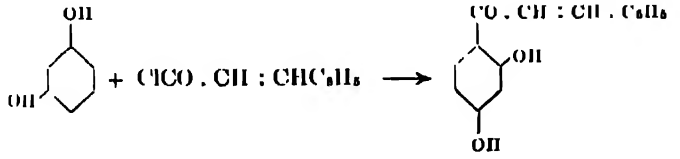
Using carbethoxyoxycinnamoyl chloride with phloroglucinol and aluminum chloride in nitrobenzene, Shinoda and Kawagoye [782] secured 5,7,4′-trihydroxyflavanone, together with two substances, m.p. 177° and 267-268°, respectively.

The condensation of most polyhydric phenols with cinnamoyl or β-phenylpropionyl chlorides in nitrobenzene under the influence of aluminum chloride at ordinary temperature leads to the formation of polyhydroxy- derivatives of phenyl styryl and phenyl β-phenylethyl ketones. With phloroglucinol, however, the isomeric flavanone derivative is the chief product.

Thus, from phloroglucinol and cinnamoyl chloride is formed 5,7-dihydroxyflavanone:



Resorcinol with cinnamoyl chloride, on the other hand, gives 2′,4′-dihydroxychalcone:



The reason that resorcinol gives chalcone derivatives, whereas phloroglucinol gives flavanone derivatives, is that the presence of the hydroxy-group at position 6 makes the 2-hydroxy- so reactive that the intermediate chalcone compound undergoes a ring closure and changes over to the flavanone derivative.

Table 15

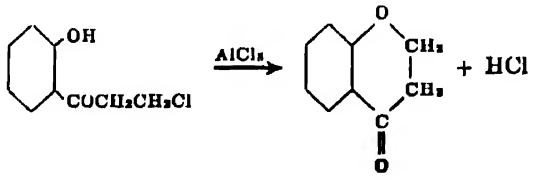
Phenol	Acid Chloride	Product	m.p. (°C)
Resorcinol	cinnamoyl	2,4-dihydroxyphenyl styryl ketone	151
Resorcinol	β-phenylpropionyl	2,4-dihydroxyphenyl β-phenylethyl ketone	84
Phloroglucinol	cinnamoyl	2,4,6-trihydroxyphenyl styryl ketone	189-190
		5,7-dihydroxyflavanone	203-204
		tricinnamoylphloroglucinol	147.5
Phloroglucinol	β-phenylpropionyl	2,4,6-trihydroxyphenyl β-phenylethyl ketone	120-121
Phloroglucinol	*p*-methoxycinnamoyl	2,4,6-trihydroxyphenyl 4-methoxystyryl ketone	176
		5,7-dihydroxy-4′-methoxyflavanone	193-194
Phloroglucinol	*p*-carbethoxycinnamoyl	5,7,4′-trihydroxyflavanone	
Phloroglucinol	3-carbethoxyoxy-4-methoxycinnamoyl	5,3,3′-trihydroxy-4′-methoxyflavanone	227-228
Phloroglucinol	*o*-methoxycinnamoyl	di-*o*-methoxycinnamoylphloroglucinol	214
		5,7-dihydroxy-2′-methoxyflavanone	224-225

[782] J. Shinoda and M. Kawagoye, *J. pharm. Soc. Japan*, 48, (560), 119-120 (1928); *Brit. Chem. Abs.*-A, 189 (1928).

Shinoda and co-workers [763] have done much work on reactions of polyhydric phenols with acyl halides for the production of chalcones or flavanones. Some of their results are summarized in Table 15.

The reaction of chloroacetyl chloride with phenol was reported by Kunckell and Johannssen.[764] Using aluminum chloride as catalyst and carbon disulfide as solvent, they could not obtain the expected *p*-ω-chloroacetylphenol; instead, with violent reaction, they secured the chloromethyl ketone of the phenyl ester of chloroacetic acid. Similarly reacting dichloroacetyl chloride with phenol they obtained the phenyl ester of dichloroacetic acid, $CHCl_2.COOC_6H_5$, m.p. 33°.

A phenyl ester was also obtained by Mayer and Zütphen when they reacted *β*-chloropropionyl chloride with phenol in the presence of aluminum chloride and carbon disulfide. The phenyl ester of *β*-chloropropionic acid (b_{12} 132-135°) was obtained in 45-50 per cent of theoretical yield. By treating the ester, under ice-cooling, with aluminum chloride, it was transformed into *o*-hydroxyphenyl *β*-chloroethyl ketone (m.p. 70°) in 40 per cent yield, and the *p*-isomer, p-hydroxyphenyl *β*-chloroethyl ketone, in about 20 per cent yield. The *o*-compound may be converted by aluminum chloride at 160-180° into chromanone (m.p. 111°) according to the equation [765]:



The Friedel-Crafts reaction of phenols with furoyl chloride has been studied by Gilman and Dickey.[766] The products from the indicated phenol and furoyl chloride with aluminum chloride are indicated:

Phenol	Solvent	Products
Phenol	CS_2	{phenyl furoate {*p*-furoylphenyl furoate
Phenol (in excess)	CS_2	phenyl furoate
Phenol	$C_6H_5NO_2$	*p*-hydroxyphenyl furoyl ketone (25%) phenyl furoate (58%)
Resorcinol	CS_2 or $C_6H_5NO_2$	2,4-dihydroxybenzoylfuran (80% yield)
Hydroquinone	CS_2 or $C_6H_5NO_2$	*p*-hydroxyphenyl furoate
Catechol		greenish blue product

Condensation of *o*-chlorophenol and benzoyl chloride in *s*-tetrachloroethane at 120-130° was shown by Hayashi [767] to give a yield of 44 per

[763] J. Shinoda and S. Sato, *J. Pharm. Soc. Japan*, 48, No. 558, 109-114; No. 560, 117-120 (1928); *Brit. Chem. Abs.*-A, 189 (1929); *J. Pharm. Soc. Japan*, 48, 791-801 (1928); *C. A.*, 23, 836 (1929); J. Shinoda, M. Kawagoye, and D. Sato, *J. Pharm. Soc. Japan*, 51, 23-25 (1931); *Brit. Chem. Abs.*-A, 1162 (1931), J. Shinoda and S. Sato, *J. Pharm. Soc. Japan*, 51, 78-82 (1931), *Brit. Chem. Abs.*-A, 1162 (1931)

[764] F. Kunckell and F. Johannssen, *Ber.*, 31, 169-171 (1898)

[765] F. Mayer and L. van Zutphen, *Ber.*, 57, 300-302 (1924), *J. Chem. Soc. Abs.*, 126 (I) 410 (1924)

[766] H. Gilman and J. B. Dickey, *Rec. trav. chim.*, 52, 389-394 (1933); *C. A.*, 27, 5073 (1933)

[767] M. Hayashi, *J. prakt. Chem.*, (1929) (n), 123, 289-312; *Brit. Chem. Abs.*-A, 89 (1930)

cent of 3-chloro-4-hydroxybenzophenone (m.p. 180-181°), a 17 per cent yield of 3-chloro-2-hydroxybenzophenone, and a 30 per cent yield of *o*-chlorophenyl benzoate. With *p*-chlorophenol and benzoyl chloride was similarly obtained an 8.5 per cent yield of 5-chloro-2-hydroxybenzophenone and a 76.5 per cent yield of *p*-chlorophenyl benzoate. *p*-Chlorophenol and *o*-toluoyl chloride similarly condensed to give a 78.7 per cent yield of *p*-chlorophenyl *o*-toluate and a 19.7 per cent yield of 5-chloro-2-hydroxyphenyl *o*-tolyl ketone.

The condensation of phthaloyl chloride with α-naphthol was studied by Csányi.[768] An *o*-phthalein becomes the chief product if α-naphthol is fused with phthaloyl chloride and aluminum chloride, treated with stannic chloride, and warmed gently. The condensation without the presence of aluminum chloride had been effected previously by Werner,[769] Sörensen and Palitzsch,[770] and other workers, who had obtained a mixture of phthaleins and phthalic ester. The formation of these products was due to the tautomeric nature of phthaloyl chloride, the symmetrical form yielding the ester, and the asymmetrical form the phthaleins. Since in ordinary phthaloyl chloride there is present only a small amount of the asymmetrical form, the tendency for the phthalate to form is predominant. If aluminum chloride is present, however, the symmetrical chloride is converted into the asymmetrical chloride and the velocity of phthalein formation becomes so great that the labile *o*-phthalein has a chance to form.

β-Naphthol with oxalyl chloride and aluminum chloride gives β-naphthofuran-1,2-dione, a yellow crystalline powder (m.p. 183°), the reaction probably occurring with primary condensation of the acid chloride with the naphthol hydroxyl, and subsequent ring closure.[771]

4-Phenanthrol undergoes Friedel-Crafts acylation, giving with propionyl chloride and aluminum chloride in nitrobenzene solution the diketone, 4-hydroxydipropionylphenanthrene (m.p. 193°) in 70 per cent yield.[772]

A series of mono- and diacylated derivatives of 2-hydroxy-9,10-dihydrophenanthrene has been prepared. The phenanthrol was treated with acetyl, propionyl, or butyryl chloride and aluminum chloride in nitrobenzene solution at low temperatures.[773]

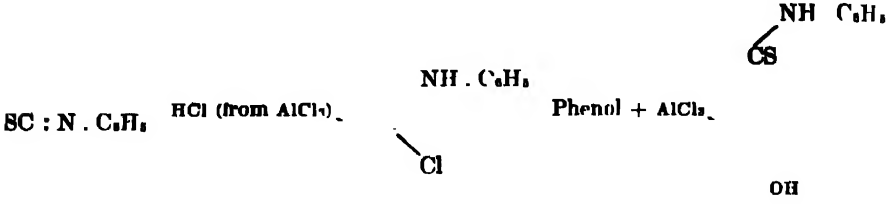
A very comprehensive patent [774] describes the condensation of chlorinated aliphatic hydrocarbons of high molecular weight with a hydroxyaromatic compound, and subsequent acylation of the resulting higher alkylated hydroxyaromatic compound with saturated or unsaturated aliphatic aromatic, and aralkyl mono- or polycarboxylic anhydrides or

[768] W. Csányi, *Ber.*, **52**, 1788-1793 (1919); *C. A.*, **14**, 1549 (1920).
[769] E. A. Werner, *J. Chem. Soc.*, **113**, 20-21 (1918).
[770] S. P. L. Sörensen and S. Palitzsch, *Biochem. Z.*, **24**, 384 (1910).
[771] Swiss P. 92,688, 93,486, and 93,489 to Herman Staudinger; *C. Z.*, 1923, II, 573. *cf.* R. Stollé, *Ber.*, **47**, 1130-1133 (1914); R. Stollé and E. Knebel, *Ber.*, **54**, 1213-1220 (1921); *J. Chem. Soc. Abs.*, **120** (I), 878.
[772] H. M. Duvall and E. Mosettig, *J. Am. Chem. Soc.*, **60**, 2409-2413 (1938).
[773] E. Mosettig and A. H. Stuart, *J. Am. Chem. Soc.*, **61**, 1-7 (1939).
[774] U. S. P. 2,138,809 (1938) to O. M. Reiff and D. E. Badertscher (to Socony-Vacuum Oil Company).

halides Aluminum chloride is used as condensing agent for both the alkylation and the acylation.

Phenols and Nitrogenous Acid Chlorides

Phenyl isothiocyanate, which in the presence of aluminum chloride reacts as the chloride of phenyl thiocarbamic acid, yields thioanilides Thus *p*-hydroxythiobenzanilide is formed from phenol and phenyl isothiocyanate.



1-Naphthol reacts in like manner, giving 1-hydroxynaphthalene-2-thioanilide.[775]

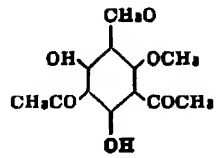
The general procedure, giving good yields, consists of grinding together the phenol, phenyl isothiocyanate, and aluminum chloride, permitting the mixture to stand for 24 hours, and then treating with water.[776] In this way an 80 per cent yield of *p*-hydroxythiobenzanilide is secured from phenol. Similarly, the following thioanilides were prepared from the indicated phenol and phenyl isothiocyanate:

Phenol	Thioanilide
o-Cresol	4-hydroxy-3-methylthiobenzanilide
m-Cresol	4-hydroxy-2-methylthiobenzanilide
p-Cresol	2-hydroxy-5-methylthiobenzanilide
Resorcinol	2,4-dihydroxythiobenzanilide
Phloroglucinol	2,4,6-trihydroxythiobenzanilide
α-Naphthol	1-hydroxy-2-thionaphthoic acid anilide
β-Naphthol	2-hydroxy-1-thionaphthoic acid anilide

Reaction of Ketones with Acyl Halides

Ease of substitution in the benzene ring depends upon the aromaticity of the component to be substituted. The presence of a ketone group in the benzene ring decreases the aromaticity of benzene, and reaction, except under extreme conditions, is totally inhibited unless there are also present several highly activating groups which may facilitate introduction of a second acyl group. Thus it is that although acylation of benzene results only in the production of monoketones, acylation of mesitylene or of durene may result in the production of diketones,[777] and like treatment of polyhydroxy- phenols often results in production of the diacyl derivatives.[778] Likewise, the three methoxy- groups and the hydroxy- group of antiarol allow a diketone to be formed,

[775] F. Mayer and A. Mombour, *Ber.*, 62, 1921-1924 (1929).
[776] H. Rivier and S. Kuss, *Helv. Chim. Acta*, 15, 379-380 (1932); *C. A.*, 26, 3280 (1932)
[777] V. Meyer and G. Pavia, *Ber.*, 29, 2564-2569 (1896)
[778] J. Shinoda and S. Sato, *J. Pharm. Soc. Japan*, 51, 78-83 (1931); *Brit. Chem. Abs.*-A, 1162 (1931).



upon condensation with acetyl chloride and aluminum chloride, cleavage of methoxy- occurring during the condensation.[779]

Reaction of *m*-xylophenone with benzoyl chloride and aluminum chloride at 170° results in formation of the diketone, 4,6-dibenzoyl-1,3-dimethylbenzene.[780] Using a temperature of 200-220°, it has been found possible to acylate even benzophenone; 1,3-dibenzoylbenzene (m.p. 100°) is formed, although in very low yield, upon treatment of the ketone with benzoyl chloride and aluminum chloride.[781]

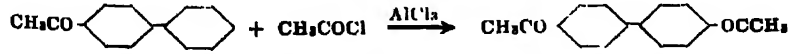
Since increased aromaticity facilitates acylation of the ketones, the presence of a ketonic group in polynuclear hydrocarbons does not inhibit further acylation. Treatment of 1-benzoylnaphthalene with benzoyl chloride and aluminum chloride at 30-35° gives a 60 per cent yield of 1,5-dibenzoylnaphthalene, together with a 20 per cent yield of the 1,8-isomeride. 1,5-Dibenzoylnaphthalene may likewise be produced by treating naphthalene with 1 molecular amount of benzoyl chloride and aluminum chloride, until evolution of hydrogen chloride has ceased, and then adding further molecular amounts of the acid halide and catalyst to the reaction mixture.[782] Or, two molecular equivalents of acid chloride and catalyst may be added primarily to naphthalene in order to secure the diketone.[783]

1-Benzoylnaphthalene with 4-chlorobenzoyl chloride similarly yields 4'-chloro-1,5-dibenzoylnaphthalene.[784]

Acylated acenaphthenes have been converted to diketones. 5-Benzoylacenaphthene with benzoyl chloride gives a 50 per cent yield of 5,6-dibenzoylacenaphthene. Likewise, 5-acetylacenaphthene and acetyl chloride in the presence of aluminum chloride gives a 70-80 per cent yield of 5,6-diacetylacenaphthene.[785]

A diacylated fluorene has been prepared by condensing benzoyl chloride with 2-benzoylfluorene and aluminum chloride. 2,7-Dibenzoylfluorene (m.p. 193-194°) was secured.

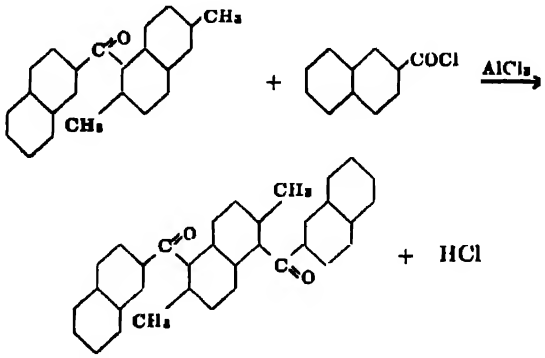
Acylated biphenyls and acyl chlorides give diacylated biphenyl derivatives. Silver and Lowy [786] obtained *p,p'*-diacetylbiphenyl from methyl *p*-xenyl ketone and acetyl chloride:



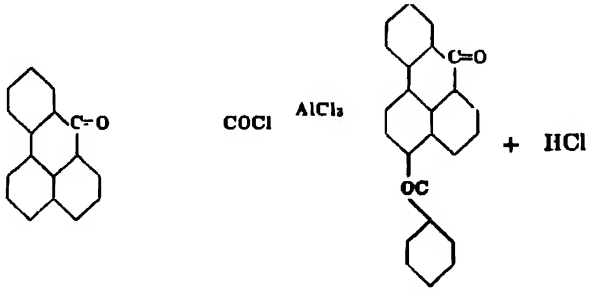
[779] E. Chapman, A. G. Perkin, and R. Robinson, *J. Chem. Soc.*, 3020 (1927).
[780] E. Clar and Fr. John, *Ber.*, 62, 3021-3029 (1929).
[781] O. Dischendorfer and A. Verdino, *Monatsh.*, 66, 255-284 (1935); *C. A.*, 30, 443.
[782] French P. 642,907 (1927); Brit. P. 279,506 (1927) to I. G. Farbenindustrie; *C. Z.*, 1929, I, 2237
[783] German P. 576,253 (1933) to I. G. Farbenindustrie; *C. A.*, 27, 3722.
[784] German P. 528,187 (1931) to I. G. Farbenindustrie; *C. Z.*, 1931, II, 1933.
[785] French P. 642,907 to I. G. Farbenindustrie (1927); *C. A.*, 23, 1417.
[786] S. L. Silver and A. Lowy, *J. Am. Chem. Soc.*, 56, 2429-2431 (1934).

In the same way, from chloromethyl *p*-xenyl ketone and chloroacetyl chloride there was obtained *p,p'*-bis-(chloroacetyl) biphenyl.

2,6-Dimethyl-1,2'-dinaphthyl ketone has been reacted with β-naphthoyl chloride and aluminum chloride to give 2,6-dimethyl-1,5-di-(2'-naphthoyl)naphthalene [787]:



Benzanthrone or its derivatives may be condensed with aroyl halides. Thus benzanthrone with benzoyl chloride gives benzoylbenzanthrone



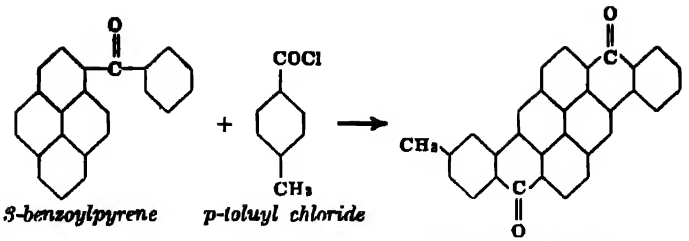
Instead of benzanthrone may be used α-hydroxybenzanthrone or benzanthronequinoline. Benzoyl chloride may be replaced with chlorobenzoyl chloride or nitrobenzoyl chloride.[788]

In the preparation of vat dyes of the anthraquinone series the treatment of pyrene ketones such as benzoylpyrene, *p*-bromobenzoylpyrene, β-naphthoylpyrene, and *p*-toluoylpyrene with aromatic acid halides in the presence of aluminum chloride for the production of diaroyl pyrenes is described. The use of aluminum chloride together with an inert fluxing agent like sodium chloride causes acylation and simultaneous dehydrogenation with ring closure to give pyranthrone derivatives [789]:

[787] L. F. Fieser and E. M. Dietz, *Ber.*, 62, 1827-1833 (1929).

[788] Brit. P. 205,502 (1923); German P. 412,053 (1924) to I. G. Farbenindustrie; *C. Z.*, 1924, I 710; *C. Z.*, 1925, I, 2063; see N. K. Moshchinskaya, *J. Gen. Chem. (U. S. S. R.)*, 9, 1276-9 (1939) *C. A.*, 34, 1663 for preparation of dibenzopyrenequinone from benzanthrone and benzoyl chloride with $AlCl_3$-NaCl.

[789] R. Scholl, K. Meyer, and J. Donat, *Ber.*, 70, 2160-2169 (1937); U. S. P. 2,072,485 (1937) to Scholl, Meyer, and Donat; *cf.* Brit. P. 459,323 (1936) to Soc. Chem. Ind. in Basle; *Brit. Chem Abs.*-B, 320 (1937).



3-benzoylpyrene *p-toluyl chloride* *methylpyranthrone*

The conversion of aryl α-naphthyl ketones into dibenzopyrenequinones by heating at 120-130° with an aroyl chloride and aluminum chloride or sodium-aluminum chloride in a current of air or oxygen is claimed in an I. G. patent.[790]

The presence of several substituents in a polynuclear ketone does not interfere with further acylation. 3,7-Diacetyl-2-hydroxy-9,10-dihydrophenanthrene is produced from acetyl chloride and the 3-acetyl derivative in the presence of aluminum chloride.[791]

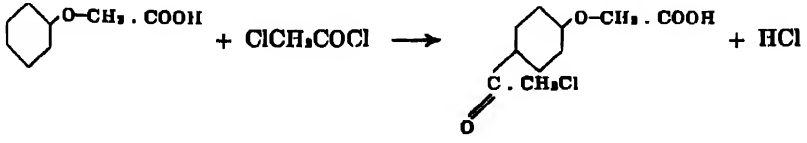
A diacylated polynuclear hydrocarbon may be further acylated. Reaction of 3,9-dibenzoylperylene with benzoyl chloride and aluminum chloride gives a tribenzoylperylene (m.p. 236-237°) in small yield.[792]

Reaction of Aromatic Carboxy- Compounds with Acid Chlorides

Although the carboxy- group has an inhibiting effect on Friedel-Crafts acylations, several instances of reactions of this type are cited in the literature. In these cases it is the presence of a strongly activating group which permits normal reaction.

Acids and Acyl Chlorides

An attempt has been made by Kunckell [793] to introduce the acetyl or chloroacetyl group into the benzene nucleus of benzoic acid by the Friedel-Crafts reaction. Although he was not successful, he did succeed in acylating phenoxyacetic acid, the reaction proceeding:



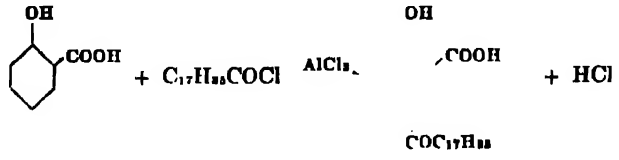
The product is *p*-(chloroacetyl)phenoxyacetic acid, m.p. 146-147°. Kunckell added 25 g of powdered aluminum chloride within a period of two minutes to a mixture consisting of 5 g of phenoxyacetic acid, 15 g

[790] British P. 294,550 (1928) to I. G.; *Brit. Chem. Abs.*-B, 637 (1929).
[791] E. Mosettig and A. H. Stuart, *J. Am. Chem. Soc.*, 61, 1-7 (1939). See also the synthesis of 4-keto-7-methoxy-8-acetyl-1,2,3,4-tetrahydrophenanthrene from 4-keto-7-methoxy-1,2,3,4-tetrahydrophenanthrene and acetyl chloride as reported by M. Miyashka and S. Nomura, *J. Pharm. Soc. Japan*, 60, 331-7 (in English, 128-31) (1940); *C. A.*, 34, 7289.
[792] A. Zinke and E. Gesell, *Monatsh.*, 67, 187-192 (1936); *C. A.*, 30, 2959.
[793] F. Kunckell, *Ber.*, 38, 2609-2611 (1905).

of chloroacetyl chloride, and 20 g of carbon disulfide. The reaction occurred immediately, and the entire mass became solid. The reaction flask was then placed in almost boiling water and within about thirty minutes a part of the reaction mass liquefied. The product is obtained by the usual decomposition of the catalyst complex and recrystallization from hot water.

Here not only the presence of the ether linkage but also the aralkyl character of the acid permits reaction. Thus, in spite of the fact that ethyl benzoate is acylated difficultly, if at all, ethyl phenylacetate easily undergoes Friedel-Crafts acylation.[794]

An unusual reaction is the condensation of salicylic acid with stearoyl chloride to give 5-stearoyl-2-hydroxybenzoic acid (m.p. 117-119°) according to the scheme:



The reaction, effected in 5 parts of nitrobenzene solution, takes place smoothly.[795] The method used resembles that of Behn [796] and of Rosenmund and Schnurr [797] for the acylation of phenols; hence esterification of the hydroxyl is prevented. The presence of the hydroxy- group activates the condensation.

Esters and Acyl Halides

Acylation of esters presents the same difficulty as it does in the case of acids. Unless the ester possesses superaromatic properties, that is, unless the electronegativity of the ester is increased by the presence of strongly electronegative groups, Friedel-Crafts acylation does not occur. In the few instances in which condensation of an ester of unsubstituted benzoic acid with an acyl halide is cited, hydrolysis of the ester occurs. Esterification of the resulting hydroxy- compound then occurs; or more rarely, the product is an acyl derivative of the phenol. A study of the mechanism of such reactions is further complicated by the possibility that the hydroxy- ketones obtained may have been formed by Fries rearrangement.

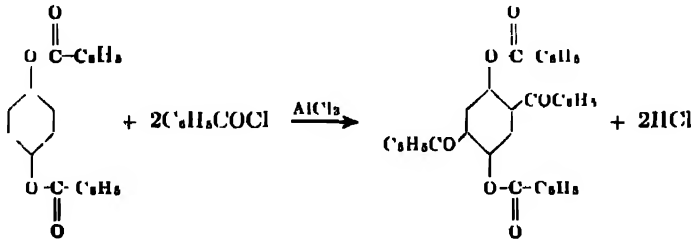
In 1883, Senff,[798] reported that the reaction of benzoyl chloride on ethyl benzoate gives *m*-benzoylbenzoic acid:

$$C_6H_5COCl \xrightarrow{C_6H_5COOC_2H_5 + AlCl_3} C_6H_5CO \cdot C_6H_4 \cdot COOH$$

[794] F. Kunckell, *Ber.*, **36**, 2609-2611 (1905).
[795] F. Seidel and O. Engelfried, *Ber.*, **69**, 2567-2581 (1936). For reaction of *m*-methoxybenzoic acid with phthaloyl chloride, see R. Weiss and W. Knapp, *Monatsh.*, **50**, 10-15 (1928); *C. A.*, **22**, 3651.
[796] German P. 95,901 (1897) to Richard Behn; *C. Z.*, 1898, I, 1223.
[797] K. W. Rosenmund and W. Schnurr, *Ann.*, **460**, 56-96 (1928); *C. A.*, **22**, 1570.
[798] P. Senff, *Ann.*, **220**, 255-258 (1883).

Here the aluminum chloride reaction complex first formed was treated with dilute sodium hydroxide to effect saponification. The yield of *m*-benzoylbenzoic acid was very small; the benzoyl chloride seemed to condense with itself.

In 1879, Doebner and Wolff [799] reported that condensation of hydroquinone with benzoyl chloride gives hydroquinone dibenzoate which, upon subsequent reaction with benzoyl chloride and aluminum chloride at 190-200° without a solvent, yields 2,5-dibenzoylhydroquinone dibenzoate, probably according to the scheme:



The diacylated dibenzoate, however, was not isolated, since it could not be crystallized. Saponification of the crude reaction products gave the dibenzoylhydroquinone, so that intermediate formation of the acylated ester was assumed.

More recent work shows that in the acylation of hydroquinone dibenzoate, saponification of the ester occurs during the reaction. Thus Finzi [800] reports the production of monobenzoylhydroquinone by treatment of the dibenzoate with benzoyl chloride and aluminum chloride in nitrobenzene solution. Bogert and Howells [801] were unable to repeat Finzi's results. They were also unable to duplicate the work of Doebner and Wolff, securing in the condensation of hydroquinone dibenzoate and two moles of benzoyl chloride with aluminum chloride only about a 2 per cent yield of dibenzoylhydroquinone. By maintaining the temperature at 200-205°, however, and adding the catalyst in small portions over a period of 48 hours, a 12-15 per cent yield of dibenzoylhydroquinone was obtained. According to Dischendorfer and Verdino [802] the diketone is probably 2,6-dibenzoylhydroquinone.

Reaction of phenyl acetate with *o*-phthaloyl chloride and aluminum chloride does not yield the acylated ester. Instead, a little phenolphthalein, *sym*-diphenylphthalate, and a gum are secured.[803]

The ester is also hydrolyzed in the condensation of phenyl benzoate with furoyl chloride and aluminum chloride in nitrobenzene. Here

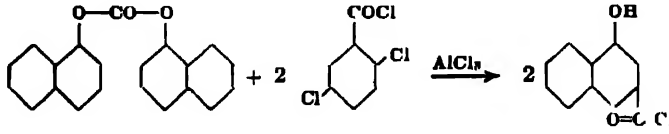
[799] O. Doebner and M. Wolff, *Ber.*, 12, 661-663 (1879).
[800] F. Finzi, *Monatsh.*, 26, 1119-1138 (1905).
[801] M. T. Bogert and H. P. Howells, *J. Am. Chem. Soc.*, 52, 837-850 (1930).
[802] O. Dischendorfer and A. Verdino, *Monatsh.*, 66, 255-284 (1935); *C. A.*, 30, 443.
[803] W. Knapp, *Monatsh.*, 58, 176-182 (1931); *Brit. Chem. Abs.*-A, 1292 (1931). For reaction with methyl *m*-methoxybenzoate, see R. Weiss and W. Knapp, *Monatsh.*, 50, 10-15 (1928); *C. A.*, 22, 3851.

p-hydroxyphenyl furoyl ketone is secured in 32 per cent yield. Only a 7 per cent yield was obtained by using carbon disulfide as solvent.[804]

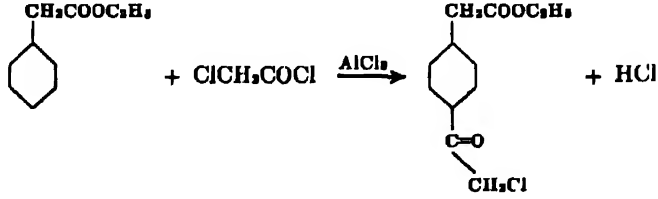
α- or *β*-Dinaphthyl carbonate has been condensed with carboxylic acid chlorides in the presence of aluminum chloride.[805]

Benzoyl chloride with *β*-dinaphthyl carbonate and aluminum chloride in tetrachloroethane at 40-70° yields hydroxynaphthyl phenyl ketone, m.p. 172-173°. Here cleavage of the dinaphthyl carbonate results, and the product is the acyl derivative of the resulting naphthol.

The reaction may likewise be effected with chloro-substituted benzoyl chloride:



With esters of aralkyl acids, however, acylation without ester hydrolysis is obtained. Kunckell [806] describes an acylation of the ethyl ester of phenylacetic acid. He slowly treated a mixture consisting of 7 g of the ester, 15 g of chloroacetyl chloride and 25 g of carbon disulfide with 25 g of powdered aluminum chloride. Reaction begins immediately and is completed in two hours. It takes the following course:

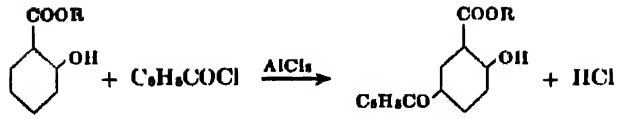


The product is the ethyl ester of *p*-(chloroacetyl)phenylacetic acid (m.p. 56-58°), which is obtained in good yield. According to Kunckell, not only halogenated acid chlorides, but also non-substituted acid chlorides or bromides may be used in the reaction.

An *o*-hydroxy- group is sufficiently activating to permit normal Friedel-Crafts acylation.

The reaction of benzoyl chloride with esters of salicylic acid was studied by Limpricht [807] who reported that the reaction proceeds according to the equation:

[804] H. Gilman and J. B. Dickey, *Rec. trav. chim.*, 52, 389-394 (1933); *C. A.*, 27, 3073
[805] German P. 530,860 (1929) to I. G. Farbenindustrie, *C. A.*, 25, 3358
[806] F. Kunckell, *Ber.*, 33, 2609-2611 (1905).
[807] H. Limpricht, *Ann.*, 290, 164-171 (1896).

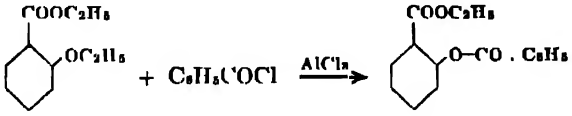


A mixture of equivalent amounts of benzoyl chloride and the salicylate in carbon disulfide was slowly dropped into aluminum chloride in the same solvent. Using this method the following products were obtained:

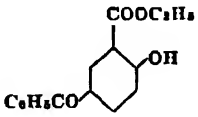
methyl 5-benzoylsalicylate, $C_6H_5.CO.C_6H_3(OH).COOCH_3$, m.p. 92°
ethyl 5-benzoylsalicylate, $C_6H_5.CO.C_6H_3(OH).COOC_2H_5$, m.p. 97°
phenyl 5-benzoylsalicylate, $C_6H_5.CO.C_6H_3(OH).COOC_6H_5$, m.p. 84°

m-Nitrobenzoyl chloride with salicylates was found to react similarly.

Upon treating the ethyl ether of ethyl salicylate with benzoyl chloride and aluminum chloride in carbon disulfide, the following reaction occurred:

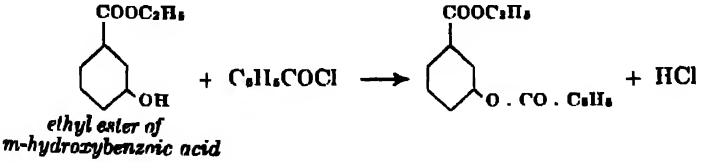


The diester obtained melts at 79°. At the same time ethyl 5-benzoylsalicylate (m.p. 97°)



is also formed. Obviously, cleavage of the ethoxy group occurred during the reaction, and some of the benzoyl chloride reacted with the resulting hydroxy- group to give the benzoate.

The same type of reaction also took place when the ethyl ester of *m*-hydroxybenzoic acid or the ethyl ester of *m*-ethoxybenzoic acid was treated with benzoyl chloride and aluminum chloride:



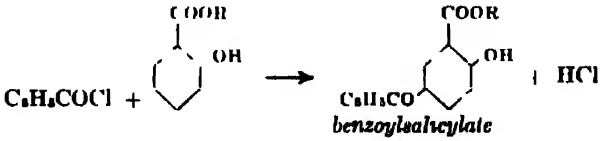
ethyl ester of m-hydroxybenzoic acid

A ketone could not be prepared by this method.

In a subsequent study of the action of benzoyl chloride and phthaloyl chloride on esters of the three hydroxybenzoic acids, Limpricht [808] summarized their different behaviors as follows:

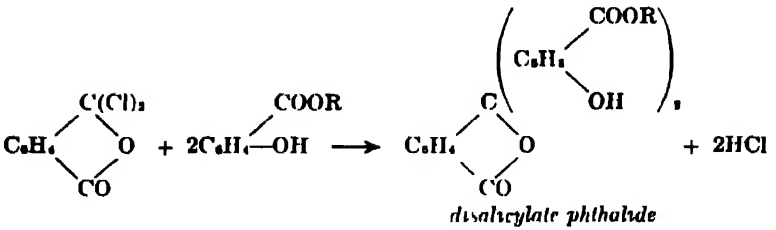
(1) With the esters of *o*-hydroxybenzoic acid regular acylation occurs, the chlorine of the acyl chloride uniting with a hydrogen from the benzene nucleus:

[808] H. Limpricht, *Ann.*, 303, 274-289 (1898).



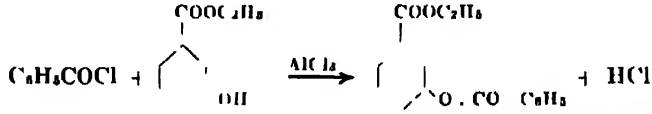
benzoylsalicylate

or,

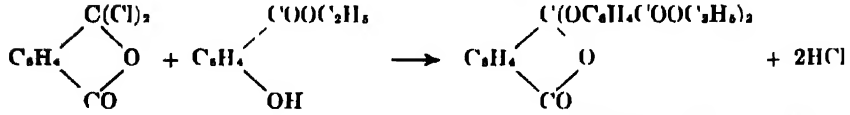


disalicylate phthalide

(2) With *m*- or *p*-hydroxybenzoates, the phenolic hydrogen unites with the chlorine of the acid chloride:



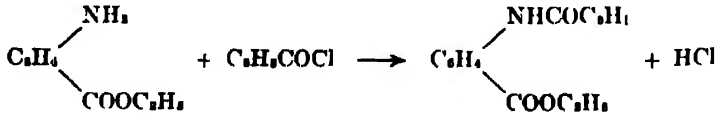
benzoylaminobenzoic acid ethyl ester

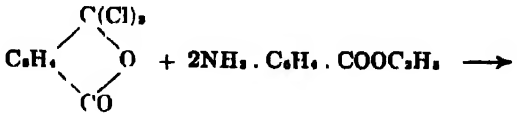


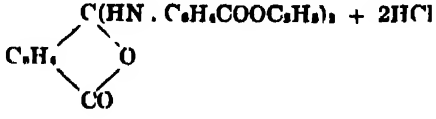
phthaloyloxybenzoic acid ethyl ester

According to Limpricht, phthalic anhydride does not react with salicylates with formation of phthalyl compounds.

The action of benzoyl or phthaloyl chlorides on *m*-, and *p*-aminobenzoic acid ethyl esters in the presence of aluminum chloride was also studied. It was found that the N-hydrogen was replaced by the acyl residue:





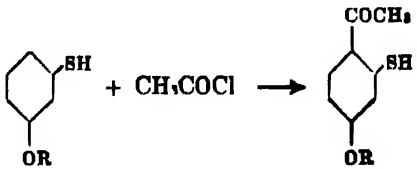


Methyl *p*-orsellinate dimethyl ether has been reported to undergo normal Friedel-Crafts acylation with acetyl chloride and aluminum chloride in nitrobenzene solution to yield methyl 6-methylresacetophenone-3-carboxylate-4-methyl ether. Here a number of activating groups permit reaction.[809]

Reaction of Organic Sulfur Compounds with Acid Halides

Thiophenols and Thiophenol Ethers

Although Friedel-Crafts acylation of thiophenol has not been reported, alkoxy- derivatives of thiophenol readily undergo the reaction. Thus 3-methoxy- or ethoxythiophenol with acetyl chloride and aluminum chloride in carbon disulfide yield normal acylation products [810]:



Introduction of a methyl group instead of the alkoxy- group into the nucleus does not have a sufficiently activating effect to permit reaction, for no condensation occurs with *p*-thiocresol and acetyl chloride under the same conditions.[811]

As the aromaticity of the thiophenol and the activity of the acid chloride are increased, however, condensation occurs more readily. Reaction of β-thionaphthol with oxalyl chloride and aluminum chloride results in the production of β-naphthathiofuran-1,2-dione, m.p. 153°. The reaction probably proceeded through the intermediate introduction of the COCOCl group, and subsequent ring closure.[812]

Increasing the aromaticity of the thiophenol through etherification likewise permits condensation. Thiophenol ethers are easily acylated. Condensation of the ethyl ether of thiophenol with benzoyl chloride in carbon disulfide at ordinary temperature results in an 80-85 per cent of theoretical yield of phenoxyphenyl ethyl sulfide, m.p. 82-83°:

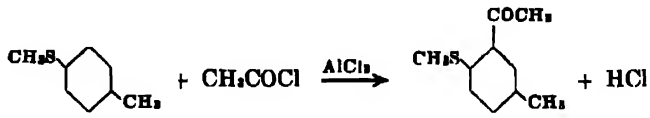
$$C_6H_5S.C_6H_5 + C_6H_5COCl \qquad C_6H_5S.C_6H_4.CO.C_6H_5 + HCl$$

A like reaction occurs when benzoyl chloride is replaced by acetyl chloride.[813]

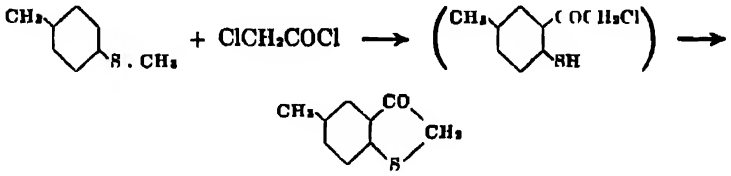
Condensation of thiophenol methyl ether with *o*-phthaloyl chloride and aluminum chloride in carbon disulfide proceeds with formation of thiophenolphthalein dimethyl ether (m.p. 99-100°) which is secured in

50 per cent yield.[814] Like treatment of the methyl ether of *p*-bromothiophenol, however, gives 2',7'-dibromo-1-thiofluoran (m.p. 214-216°) in 15 per cent yield.[815]

As would be expected, ethers of alkylated thiophenols undergo Friedel-Crafts acylation even more readily than do the corresponding unsubstituted compounds. *p*-Tolyl methyl sulfide, for example, reacts with acetyl chloride to give almost a quantitative yield of 2-acetyl-4-methylphenyl methyl sulfide (m.p. 51.5°) according to the scheme[816]:



Reaction of *p*-tolyl methyl sulfide with chloroacetyl chloride and aluminum chloride, on the other hand, results in the formation of 4-methyl-2-ketodihydrothionaphthene (m.p. 102°) in a 50 per cent of theoretical yield. The reaction probably proceeded with intermediate formation of *o*-(chloroacetyl)*p*-thiocresol, but this primary product could not be isolated. Cleavage of the ether linkage also occurred during the condensation, the final product being formed according to the scheme:



Ring closure is also effected in the condensation of *p*-tolyl methyl sulfide with *o*-phthaloyl chloride and aluminum chloride. Here 2',7'-dimethyl-1-thiofluoran is obtained in 55 per cent yield.[817]

Diphenyl sulfide condenses with oxalyl chloride with substitution of both chlorine atoms to give 4,4'-diphenylthiolbenzil [818]

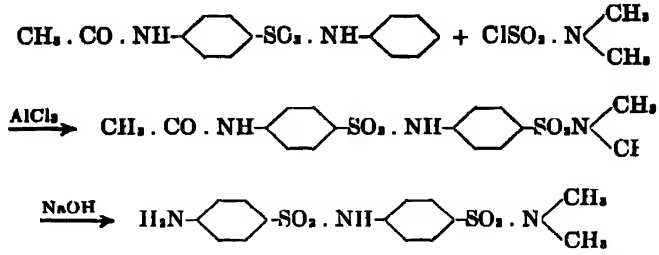
$$ClCO \cdot COCl + 2C_6H_5 \cdot S \cdot C_6H_5 \xrightarrow{AlCl_3} C_6H_5 \cdot S \cdot C_6H_4 \cdot CO \cdot CO \cdot C_6H_4 \cdot S \cdot C_6H_5 + 2HCl$$

Thiophenol ethers, like phenol ethers, condense readily with carbamyl chloride with production of the corresponding acid amides,[819] the reaction with thiophenol ethyl ether proceeding:

$$C_2H_5 \cdot S \cdot C_6H_5 + ClCONH_2 \xrightarrow{AlCl_3} C_2H_5 \cdot S \cdot C_6H_4 \cdot CO \cdot NH_2 + HCl$$

[814] W. Knapp, *Monatsh.*, **56**, 66-70 (1930); *C. A.*, **24**, 5034.
[815] W. Knapp, *Monatsh.*, **56**, 106-112 (1930); *C. A.*, **24**, 5034.
[816] K. v. Auwers and F. Arndt, *Ber.*, **42**, 537-545 (1909); *J. Chem. Soc. Abs.*, **96** (I), 175 (1909).
[817] R. Weiss and W. Knapp, *Monatsh.*, **50**, 392-398 (1928); *C. A.*, **23**, 1896.
[818] W. Dilthey, O. Trösken, K. Plum and W. Schommer, *J. prakt. Chem.*, **141**, 331-349 (1934).
[819] K. v. Auwers and C. Beger, *Ber.*, **27**, 1733-1741 (1894).

Kranzlein [820] has indicated the possible usefulness of N-acylated aromatic amines in the preparation of therapeutically active sulfanilamides. Thus, condensation of 4-acetylaminobenzosulfanilide with dimethylamino-N-sulfochloride yields 4'-acetylaminobenzosulfaniline-4-dimethylsulfamide, which upon saponification gives 4'-aminobenzosulfaniline-4-dimethylsulfamide:

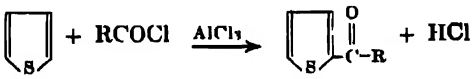


The final product compares very favorably with medicinals of the Prontosil type.

Heterocyclic Compounds of Sulfur

Thiophene

Thiophene is one of the most easily substituted ring compounds; hence it enters readily into Friedel-Crafts reactions with acid chlorides to give mono-acyl substituents in the 2-position:



The use of aluminum chloride as catalyst in this synthesis has not been very generally accepted because it entails strict observance of detail in experimental conditions. Thus, Minnis [821] points out that thiophene and aluminum chloride react vigorously in carbon disulfide suspension. In the preparation of phenyl thienyl ketone, he secured 88-90 per cent yields if a solution of benzoyl chloride and thiophene in carbon disulfide is added to a suspension of aluminum chloride in the same solvent. If, however, a carbon disulfide solution of the acid chloride was added to a suspension of thiophene and aluminum chloride, much tar was formed, and a low yield of the ketone resulted.

The preparation of phenyl thienyl ketone had been first reported by Comey,[822] who had treated a mixture of crude thiophene and benzoyl chloride with aluminum chloride. Comey noticed the evolution of hydrogen sulfide during the reaction. The preparation was repeated by Marcusson,[823] who recommended that an excess of benzoyl chloride be employed, and that heating be dispensed with. According to Ernst,[824] the use of an excess of solvent was found to be advantageous in the

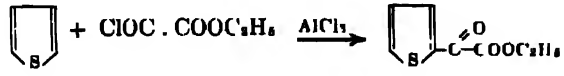
[820] P. Kranzlein, *Z. ang. chemie.*, 51, 373-381 (1938).
[821] W. Minnis, *Organic Syntheses*, 12, 62 (1932).
[822] A. Comey, *Ber.*, 17, 790-791 (1884).
[823] J. Marcusson, *Ber.*, 26, 2457-2465 (1893).
[824] F. Ernst, *Ber.*, 19, 3278-3282 (1886).

reaction. He readily obtained tolyl thienyl ketone by the action of *o*-toluyl chloride on thiophene in ten times the volume of petroleum ether with aluminum chloride.

Obviously, these early workers were attempting to mitigate the action of aluminum chloride on toluene. This same development is seen in the reaction of aliphatic acid chlorides with thiophene. The preparation of methyl thienyl ketone was first reported by Peter,[825] who dissolved thiophene and acetyl chloride in petroleum ether and treated the resulting solution with aluminum chloride. He secured a 50 per cent of theoretical yield of the ketone. The same method was used by Krekeler [826] in the preparation of ethyl or propyl thienyl ketones, and by Schleicher [827] in the preparation of hexyl thienyl ketone.

Biedermann [828] secured a 90 per cent yield of methyl thienyl ketone by adding 150 g of aluminum chloride to a solution of 50 g of thiophene and 55 g of acetyl chloride in 550 g of light petroleum. After hydrogen chloride was no longer evolved, even upon heating, the solvent was decanted and the residue again treated with 5 g of acetyl chloride and aluminum chloride. Here, it is noticed the catalyst did not come into contact with the thiophene previous to the reaction. Subsequently, Bradley [829] improved this procedure to secure an especially pure product by adding a solution of thiophene and acetyl chloride in petroleum ether very slowly to aluminum chloride suspended in an excess of the same solvent Except for the use of carbon disulfide instead of petroleum ether as solvent, this is the procedure which was used by Minnis [821] in his preparation of phenyl thienyl ketone.

The same procedure has also been used by Steinkopf and Wolfram [830] in the preparation of ethyl thienyl-2-glyoxylate. Here one mole of thiophene and one mole of the ethyl chloroglyoxylate in five times the volume of petroleum ether were added with stirring to one mole of aluminum chloride also in five times its volume of petroleum ether. The yields of ethyl thienyl-2-glyoxylate thus prepared ranged from 47.5 to 57 per cent of the theoretical. The reaction is similar to that of the preparation of ethyl phenylglyoxylate, as described by Bouveault.[831] It proceeds probably according to the equation:



The condensation of thiophene with diethylmalonyl chloride has been investigated by Freund and Fleischer [832] Although aromatic hydrocarbons under the same conditions condense with alkyl-malonyl chlorides to

[825] A. Peter, *Ber.*, 17, 2643-2647 (1884).
[826] K. Krekeler, *Ber.*, 19, 674-679 (1886).
[827] E. Schleicher, *Ber*, 19, 860-870 (1886).
[828] A. Biedermann, *Ber*, 19, 836-840 (1886).
[829] W P Bradley, *Ber*, 19, 2113-2123 (1886)
[830] W. Steinkopf and A. Wolfram, *Ann*, 437, 23-36 (1924)
[831] L. Bouveault, *Bull. soc chim (3)*, 15, 1014-1021 (1896).
[832] M. Freund and K. Fleischer, *Ann*, 373, 291-336 (1910); *J. Chem. Soc Abs*, 98 (I), 490 (1910)

give indandiones, with thiophene ring closure does not occur, the product being a mixture of diethylthiophenoylmethane (m.p. 146-147°) and diethyldithiophenoylmethane, m.p. 152-153°.

Steinkopf and his co-workers preferred to use phosphorus pentoxide as catalyst in the synthesis of thienyl ketones from thiophene and acid chloride or acid anhydride.[833] By this method they secured from propionyl chloride and thiophene a 42 per cent yield of 2-propiothienone. 2-Isovalerothienone was prepared in 67 per cent yield using the corresponding acid chloride.

Recent literature [834] indicates interest in the use of stannic chloride as catalyst in the reaction. Phenyl thienyl ketone is reported to be prepared in 82.5-92 per cent yield by this method, and methyl thienyl ketone in 96 per cent yield. Stannic chloride has also been claimed as catalyst in the production of thienyl alkyl ketones by reaction of thiophene with acid chlorides of 11-17 carbon atoms.[835]

Much work has been done on the acylation of halogenated thiophenes. Gattermann and Römer [836] acetylated 2- and 2,5-bromo- or iodothiophenes and concluded that in the acylation of the dihalogenated derivatives, the acetyl group displaces one of the halogen atoms, thus yielding the same compound as is obtained by acetylating the monohalogenated derivative. In both cases the product was 5-halogeno-2-acetylthiophene. Steinkopf and Jacob,[837] however, report that the reaction of 2,5-dibromothiophene, acetyl chloride, and aluminum chloride gives 2,5-dibromo-3-acetothienone. Steinkopf and co-workers have reacted acetyl chloride and benzoyl chloride with various mono-, di-, tri-, and tetrahalogenated thiophenes in the presence of aluminum chloride.[838]

The reaction of a number of brominated methyl- and ethylthiophenes with acyl chlorides in the presence of aluminum chloride has been studied by Steinkopf.[839] Demuth [840] has described the acetylation of iodoethylthiophene.

The reaction of alkylated thiophenes with acid chlorides in the presence of aluminum chloride proceeds quite regularly. Some acylations of alkyl thiophenes are listed in Table 16.

In the reaction of thiophenyl acetate with phthaloyl chloride and aluminum chloride, hydrolysis of the ester occurs, with formation of *asym*-diphenyl dithiophthalate.[841] In spite of the fact that substitution in the thiophene series occurs more readily than in the benzene series, here, too, the presence of the carboxy- group inhibits acylation.

The reaction of carbamyl chloride with compounds of the thiophene series in the presence of aluminum chloride has been investigated by

[833] W. Steinkopf and I. Schubart, *Ann.*, 424, 1-23 (1921).
[834] *cf.* G. Stadnikoff and I. Goldfarb, *Ber.*, 61, 2341-2342 (1928).
[835] U. S. P. 2,101,560 (1936) to A. W. Ralston (to Armour and Co.).
[836] L. Gattermann and M. Römer, *Ber.*, 19, 688-695 (1886).
[837] W. Steinkopf and H. Jacob, *Ann.*, 515, 273-283 (1935).
[838] *cf.* W. Steinkopf, H. Jacob, and H. Penn, *Ann.*, 512, 136-164 (1934).
[839] W. Steinkopf, *Ann.*, 513, 281-294 (1934); *Ann.*, 515, 273-282 (1935).
[840] R. Demuth, *Ber.*, 19, 679-686 (1886).
[841] W. Knapp, *Monatsh.*, 52, 176-182 (1931); *Brit. Chem. Abs.*-A, 1292 (1931).

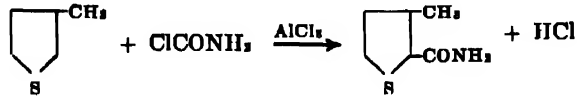
Table 16

Alkylated thiophene	Acid Chloride	Product	Ref.
3-Methyl	acetyl	3-methyl-2-acetylthiophene	1, 2
2-Methyl	acetyl	2-methyl-5-acetylthiophene	3
3-Methyl	benzoyl	3-methylthienyl 5-phenyl ketone 3-methylthienyl 2-phenyl ketone	13
2-Ethyl	benzoyl	2-ethyl-5-benzoylthiophene	11
2-Ethyl	acetyl	5-ethyl-2-acetylthiophene	8
3-Ethyl	acetyl	3-ethyl-2-acetylthiophene	3
Ethyl	oenanthylic	ethylthienyl hexyl ketone	8
2-Propyl	acetyl	5-propyl-2-acetylthiophene	5
3-Isopropyl	acetyl	3-(or 4)-isopropyl-2-acetylthiophene	6
2-*n*-Octyl	acetyl	5-*n*-octyl-2-acetylthiophene	7
2,5-Dimethyl	acetyl	2,5-dimethyl-3-acetylthiophene	5, 10
2,5-Dimethyl	benzoyl	2,5-dimethyl-3-benzoylthiophene	4
Diethyl	acetyl	acetyldiethylthiophene	9

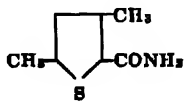
References

1. R. Demuth, *Ber.*, **18**, 3024-3026 (1885).
2. M. Gerisch, *Ann.*, **267**, 145-170 (1892).
3. R. Demuth, *Ber.*, **19**, 1859-1861 (1886)
4. M. Kitt, *Ber.*, **28**, 1807-1814 (1895).
5. H. Ruff, *Ber.*, **20**, 1740-1750 (1887).
6. A. Thiele, *Ann.*, **267**, 133-138 (1892).
7. E. von Schweinitz, *Ber.*, **19**, 644-649 (1886).
8. E. Schleicher, *Ber.*, **18**, 3015-3023 (1885); *Ber*, **19**, 660-670 (1886)
9. F. Muhlert, *Ber.*, **19**, 633-636 (1886).
10. F. Silberfarb, *J. Russ. Phys.-Chem. Soc.*, **45**, 1936-1940 (1913); *C. Z*, 1914, I, 1663
11. J. Marcusson, *Ber.*, **26**, 2457-2465 (1893).

Gattermann.[842] With 3-methylthiophene it yields the amide of 3-methylthiophene-2-carboxylic acid, m.p. 119°:



With 3,4-dimethylthiophene, carbamyl chloride gives the amide of 3,4-dimethylthiophene-2-carboxylic acid, m.p. 115-116°:



Trimethylthiophene reacts similarly, giving trimethylthiophenic acid amide, m.p. 146-147°.

In 1885, Leuckart and Schmidt [843] reported that thiophene with phenyl isocyanate yielded the anilide, $C_4SH_3 . CO . NHC_6H_5$, the reaction taking place with intermediate formation of phenylcarbamyl chloride (from phenyl isocyanate and hydrogen chloride evolved by aluminum chloride) and subsequent reaction of the acid chloride with thiophene. Gattermann's work on carbamyl chloride with thiophene derivatives [842] was based on this reaction.

[842] L. Gattermann, *Ann.*, **244**, 29-76 (1888).
[843] R. Leuckart and M. Schmidt, *Ber.*, **18**, 2338-2341 (1885); *J. Chem. Soc. Abs.*, **48**, 1234 (1885).

Miscellaneous Heterocyclic Compounds of Sulfur

Other sulfur-containing heterocyclic compounds have been acylated in the presence of aluminum chloride. Thianaphthene and acetyl chloride with aluminum chloride in carbon disulfide gives methyl thianaphthyl ketone (m.p. 64°) in about 30 per cent yield.[844]

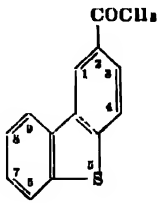
The methyl ether of 3-hydroxythianaphthene treated with the requisite acid chloride and aluminum chloride in the presence of carbon disulfide has been found to yield the following ketones [845]:

2-acetyl-3-hydroxythianaphthene, m.p. 82°
2-propionyl-3-hydroxythianaphthene, m.p. 73-74°
2-β-chloropropionyl-3-hydroxythianaphthene, m.p. 121-122°

Hydrolysis of the ether occurred during the reaction.

Thianthrene has been similarly reacted with chloroacetyl chloride. Diacylation was secured in this case, 2,6-bis-(β-chloroacetyl)thianthrene (m.p. 177°) being obtained.[846] Phenothioxin has been shown to undergo like reaction; the product with chloroacetyl chloride is 3,6-bis(β-chloroacetyl)phenothioxin (m.p. 193°) prepared in good yield.[847]

A study of the reaction of dibenzothiophene with acetyl chloride and aluminum chloride has been made by Burger and co-workers.[848] In a series of nine experiments, a mixture of ketones was obtained in every case. With nitrobenzene as solvent, and adding the catalyst to a mixture of the reactants, the main product is 2-acetyldibenzothiophene, m.p. 111-112°.



The ketone has also been prepared in 70 per cent yield by Gilman and Jacoby,[849] who used carbon disulfide as solvent. Burger and Bryant [850] have made repeated attempts to duplicate this yield, but have obtained only a mixture of ketones in 70 per cent yield. The yield of pure 2-acetyldibenzothiophene was only about 25 per cent.

Cullinane, Rees, and Plummer [851] have been unable to obtain a monoacetyl derivative by treatment of dibenzothiophene with acetyl chloride under various conditions. By using carbon disulfide as solvent and boil-

[844] G. Komppa, *J. prakt. Chem.*, 122, 319-331 (1929); *C. A.*, 24, 112 (1930).
[845] F. Krollpfeiffer and K. Schneider, *Ber.*, 61, 1284-1291 (1928).
[846] M. Tomita, *J. Pharm. Soc. Japan*, 58, 517-521 (in German, 139-141) (1938); *C. A.*, 32, 7463
[847] M. Tomita, *J. Pharm. Soc. Japan*, 58, 510-517 (in German, 136-139) (1938); *C. A.*, 32, 7467.
[848] A. Burger, W. B. Wartinen, and R. E. Lutz, *J. Am. Chem. Soc.*, 60, 2628-2630 (1938); *C. A.*, 33, 581.
[849] H. Gilman and A. L. Jacoby, *J. Org. Chem.*, 3, 108-119 (1938).
[850] A. Burger and H. W. Bryant, *J. Org. Chem.*, 4, 119-122 (1939).
[851] N. M. Cullinane, A. G. Rees, and C. A. J. Plummer, *J. Chem. Soc.*, 151-153 (1939).

ing the reaction mixture for two hours, these workers secured 1 g of 2,8-diacetyldibenzothiophene (m.p. 210°) from 5 g of dibenzothiophene.

In this connection, it is interesting that Burger, Wartman, and Lutz [848] have obtained 2,8-diacetyldibenzothiophene (m.p. 208-209°) as the main reaction product, when using boiling carbon disulfide as solvent. At the same time, however, these workers also secured a mixture of ketones, m.p. 85-100°. The structure of the 2,8-diacetyl derivative was established by conversion to the dioxime, rearrangement to the diacetamido- compound and hydrolysis to 2,8-diaminodibenzothiophene. The 2,8- compound could also be obtained in 90 per cent yield by treatment of 2-acetyldibenzothiophene with acetyl chloride and aluminum chloride.

Courtot and Pomonis [852] report the preparation of 2-acetamidobenzothiophene (m.p. 167-168°) by nitration of thiophene, subsequent reduction, and acetylation. Following the same procedure, Gilman and Jacoby [849] report that the melting point of 2-acetamidobenzothiophene obtained by them is 178°.

Heterocyclic Compounds of Oxygen and Acyl Halides

Furan

Furan chemistry is of recent date. Since about 1930 much work has been done on Friedel-Crafts reactions with furan and its derivatives, but the greater part of it has dealt with Friedel-Crafts alkylations. Aluminum chloride is one of the less efficient catalysts for acylating furans.

According to Gilman and Burtner [853] the general order of decreasing usefulness of condensing agents in acylations of furan is: stannic chloride,

Table 17

Furan	Acid Chloride	Product	% Yield	Ref
Furan	chloroacetyl	2-(ω-chloroacetyl)furan	21	1
Furan	propionyl	2-propionylfuran	37.6	2
Furan	*n*-propionyl	2-propionylfuran	36.3	4
Furan	*n*-butyryl	2-butyrylfuran	51.8	4
Furan	isobutyryl	2-isobutyrylfuran	45.3	4
Furan	*n*-valeryl	2-*n*-valerylfuran	23	4
Furan	*n*-caproyl	2-*n*-caproylfuran	39	4
Furan	lauroyl	furyl undecyl ketone		5
Furan	stearoyl	furyl heptadecyl ketone		5
Furan	2-furoyl	di-α-furyl ketone	very low	3
5-Methylfuran	acetyl	5-methyl-2-acetylfuran	12	3
2-Methylfuran	acetyl	2-methyl-5-acetylfuran	28.3	2
2,5-Dimethylfuran	benzoyl	2,5-dimethyl-3-benzoylfuran	7	4
Methylfuran	stearoyl	methylfuryl heptadecyl ketone		

References

1. H. Gilman and R. R. Burtner, *J. Am. Chem Soc*, 57, 909-912 (1935).
2. N. I. Shukin, E. V. Shemastina, and E. D. Cherkasova, *J. Gen. Chem. (U. S. S. R.)*, 5, 674-679 (1935); *C. A.*, 33, 1816
3. T. Reichstein, *Helv. Chim. Acta*, 13, 356-360 (1930); *C. A.*, 24, 2781; *C. Z.*, 1930, II, 490.
4. H. Gilman and N. O. Calloway, *J. Am. Chem. Soc.*, 55, 4197-4206 (1933).
5. U. S. P. 2,038,542 (1936) to A. W. Ralston and C. W. Christensen (to Armour and Co.), *C. A.*, 30, 3124.

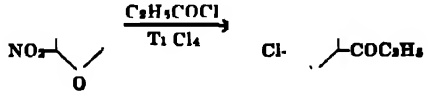
[852] C. Courtot and C. Pomonis, *Compt. rend.*, 182, 893-895 (1926); *C. A.*, 20, 2155.
[853] H. Gilman and R. R. Burtner, *J. Am. Chem. Soc.*, 57, 909-912 (1935).

ferric chloride, aluminum chloride, and titanium chloride. On the other hand, aluminum chloride is highly efficient in alkylating furans.

Some reactions of furan with acyl halides in the presence of aluminum chloride are tabulated in Table 17.

Although acylation of furoic esters has been effected in the presence of ferric chloride and of stannic chloride, aluminum chloride is ineffective in the acetylation of methyl furoate with acetyl chloride or acetic anhydride.[854]

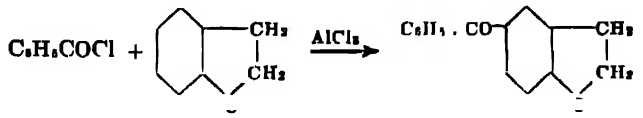
Noteworthy also is that fact that nitrofuran has been reacted with acyl halides,[855] although nitrobenzene does not undergo Friedel-Crafts acylation under any condition. 2-Nitrofuran with propionyl chloride in the presence of titanium tetrachloride and carbon disulfide yields 5-chloro-2-furyl ethyl ketone:



The fact that the nitro- group is replaced by chlorine does not make this case strictly comparable with the true acylation of nitroanisole, in which condensation of nitroanisole with acetyl chloride and aluminum chloride results in production of acetylnitroanisole.[856]

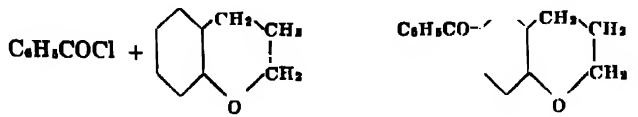
Miscellaneous Heterocyclic Compounds of Oxygen

Although Friedel-Crafts reaction of coumarone is prevented by its ready polymerization, its dihydride easily undergoes acylation. Thus, coumaran with benzoyl chloride gives 5-benzoylcoumaran (m.p. 44°):



Like reactions occur with veratroyl chloride and with trimethylgalloyl chloride.[857]

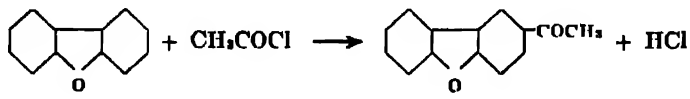
Condensation of chroman with benzoyl chloride similarly gives 6-benzoylchroman, b.p. 365°/710 mm:



[854] H. Gilman and N. O. Calloway, *J. Am. Chem. Soc.*, 55, 4197-4205 (1933).
[855] H. Gilman, R. R. Burtner, N. O. Calloway, and J. A. V. Turck, *J. Am. Chem. Soc.*, 57, 907-908 (1935).
[856] F. Stockhausen and L. Gattermann, *Ber.*, 25, 3521-3525 (1892).
[857] St. v. Kostanecki, V. Lampe, and Ch. Marschalk, *Ber.*, 40, 3660-3669 (1907); for simultaneous acylation and polymerisation of coumarone, see U. S. P. 2,189,383 (1940) to A. W. Ralston and R. J. Vander Wal (to Armour and Co.); U. S. 2,197,711 (1940) to A. W. Ralston, R. J. Vander Wal and E. W. Segebrecht (to Armour and Co.); U. S. 2,197,712 (1940) to A. W. Ralston and E. J. Hoffmann (to Armour and Co.).

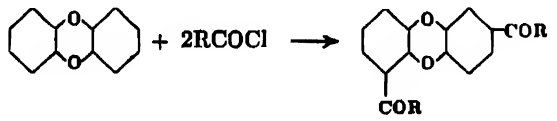
6-Veratroylchroman is secured when benzoyl chloride is replaced by veratroyl chloride in the preceding reaction.

Dibenzofuran undergoes normal acylation upon treatment with acetyl chloride and aluminum chloride in carbon disulfide solution. 3-Acetyldibenzofuran is produced according to the scheme [858]:



Like reaction occurs with benzoyl chloride,[859] and a good yield of 3-benzoyldibenzofuran (m.p. 167-168°) was obtained. Dibenzofuryl heptadecyl ketone (m.p. 83-84°) has likewise been prepared by Friedel-Crafts reaction.[860]

Diphenylene dioxide and its derivatives have been reacted with acid chlorides in the presence of anhydrous aluminum chloride and carbon disulfide to give chiefly 2,6-diacylated products:



Tomita [861] has prepared the following ketones from diphenylene dioxide and the indicated acid chloride:

Acid Chloride	Diphenylene dioxide deriv	m.p. (°C.)
Chloroacetyl chloride	2,6-bis(β-chloroacetyl)-	282
Propionyl chloride	2,6-dipropionyl	241
Chloropropionyl chloride	2,6-bis(γ-chloropropionyl)-	211 d
α-Bromopropionyl bromide	2,6-bis(β-bromopropionyl)-	213

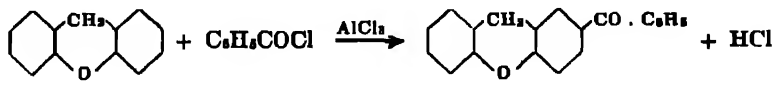
Similar reactions were found to occur with dimethyldiphenylene dioxides and acid chlorides. Methoxy- derivatives of diphenylene dioxide have also been acylated in the presence of anhydrous aluminum chloride. Thus, bis-(2-methoxyphenyl)ether and chloroacetyl chloride gives bis[2-methoxy-5(chloroacetyl)phenyl] ether, m.p. 154°.

The reaction of diphenylene oxide with at least two molecular proportions of liquid carbamyl chloride in the presence of aluminum chloride results in the formation of a diphenylene oxide dicarboxylic acid diamide, m.p. 307-308°. Instead of the liquid carbamyl chloride and aluminum

[858] P. Galewsky, *Ann.*, 264, 187-193 (1891)
[859] W. Borsche and W. Bothe, *Ber.*, 41, 1940-1944 (1908).
[860] U. S. P. 2,083,542 (1936) to A. W. Ralston and C. W. Christensen (to Armour and Co.); *C. A.*, 30, 5124.
[861] M. Tomita, *J. Pharm. Soc. Japan*, 54, 891-897 (1934); 56, 906-912 (1936); 58, 498-502 (1938); *C. A.*, 31, 109; 31, 8484; 32, 7463.

chloride, a molecular compound of the acid halide and catalyst may be used.[863]

Dibenzopyran (xanthene) is another heterocyclic compound of oxygen which undergoes ready Friedel-Crafts acylation. With benzoyl chloride, 2-benzoyldibenzopyran (m.p. 148°) is obtained[863]:



Acylation of Organic Compounds of Nitrogen by Friedel-Crafts Reaction with Acyl Halides

Friedel-Crafts acylation has not been extensively applied to organic compounds of nitrogen. With a few exceptions the presence of a nitro-group in aromatic hydrocarbons inhibits reaction, and aromatic nitriles are even more resistant to acylation. It is likewise little used in preparation of acylated amines, for substitution of N-hydrogen usually occurs in the absence of a catalyst, and indirect methods are ordinarily necessary for the introduction of an acyl group into the ring. In the acylation of acetamides, however, aluminum chloride has been found to be an especially useful catalyst.

Although heterocyclic compounds of nitrogen are generally resistant to Friedel-Crafts acylation, several instances of such reactions have been reported.

Nitro- Compounds

Although the presence of a nitro- group in aromatic hydrocarbons inhibits Friedel-Crafts ketone synthesis, the reaction may be carried out with nitro- derivatives of phenol ethers.[864] The alkoxy- group is thus sufficiently activating to allow substitution. Nitroanisole and acetyl chloride, when treated with aluminum chloride in carbon disulfide, yield acetylnitroanisole (m.p. 99.5°) together with some *o*-nitrophenol and nitrohydroxyacetophenone. The last two products are due to hydrolysis of the methoxyl group of anisole and of acetylnitroanisole, respectively. The acetyl group in the ketones probably occupies the *p*-position to the methoxy- group. *o*-Nitrophenetole reacts likewise with acetyl chloride, giving acetyl-*o*-nitrophenetole, m.p. 66-67°.

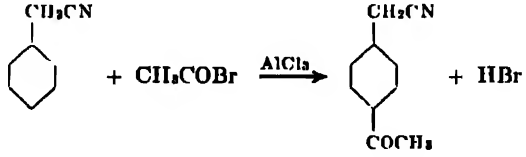
p-Nitrophenyl phenyl ether also undergoes Friedel-Crafts acylation. With stearoyl chloride, the product is *p*-nitrophenoxyphenyl heptadecyl ketone,[865] which may be used for improving motor fuels.[866]

[863] U. S. P. 2,127,257 (1938) to H. Hopff and H. Ohlinger (to I. G.); Brit. P. 456,070 (1935) to I. G., *Brit. Chem. Abs.*-B, 120 (1937); French P. 803,257 (1936) to I. G., *C. A.*, 31, 2615.
[864] J. Heller and St. v. Kostanecki, *Ber.*, 41, 1324-1329 (1908).
[865] F. Stockhausen and L. Gattermann, *Ber.*, 25, 3521-3525 (1892).
[866] U. S. P. 2,033,540 (1936) to A. W. Ralston and C. W. Christensen (to Armour and Co.); *C. A.*, 30, 3123.
[867] U. S. P. 2,100,257 (1937) to V. Conquest (to Armour and Co.); *C. Z.*, 1938, I, 3997.

Nitriles

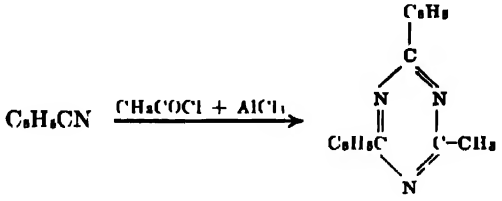
Although aromatic nitriles resist Friedel-Crafts acylation, an aralkyl nitrile may undergo the reaction.

Thus phenacetonitrile with acetyl bromide and aluminum chloride in carbon disulfide gives *p*-acetylphenacetonitrile:

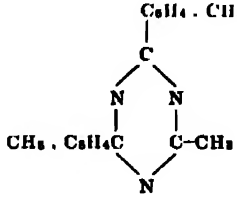


The *meta*-isomer is obtained as a by-product in the reaction.[867]

Aromatic nitriles react with acid chlorides in the presence of aluminum chloride to give triazines. Thus benzonitrile and acetyl chloride give about a 16 per cent yield of 2-methyl-4,6-diphenyl-1,3,5-triazine



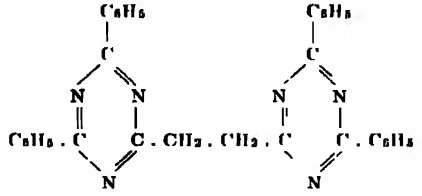
An analogous condensation occurs when propionyl, butyryl, heptoyl, or palmitoyl chloride is substituted for acetyl chloride in the foregoing reaction with formation of ethyl-, propyl-, hexyl-, or pentadecyldiphenyl triazine.[868] Acid chlorides of 7 to 9 carbon atoms likewise give the corresponding triazines.[869] That the reaction is general for aromatic nitriles is evident from the fact that *p*-tolunitrile undergoes similar reaction. Upon treatment of a mixture of *p*-tolunitrile and acetyl chloride with aluminum chloride at 0°, and subsequent heating on a water-bath for twelve hours at 70°, a very good yield of 2-methyl-4,6-di-*p*-tolyl-1,3,5-triazine,



is reported. When an aromatic nitrile is reacted with a dicarboxylic acid chloride, a two-ringed compound is formed: benzonitrile and succinyl

[867] F. Kunckell, *Ber.*, 39, 3145-3148 (1906)
[868] F. Krafft and A. von Hansen, *Ber.*, 22, 803-811 (1889).
[869] F. Krafft and G. Koenig, *Ber.*, 23, 2382-2388 (1890).

chloride with aluminum chloride at 100° give 2,2'-ethylene-bis-(4,6-diphenyl-1,3,5-triazine)[869]:



Triazines are not formed when aromatic acid chlorides are used. Treatment of benzonitrile with benzoyl chloride and aluminum chloride yields dibenzamide [870]:

$$C_6H_5CN \xrightarrow[AlCl_3]{C_6H_5COCl} (C_6H_5CO)_2NH$$

Amines

Aluminum chloride has been little used in condensation of aromatic amines with acyl halides. It is not needed in replacement of N-hydrogen with acyl, and attempts to use the catalyst in introduction of an acyl group into the ring of N-dialkyl amines have not met with great success because of formation of complex condensation products.

The condensation proceeds more readily with aliphatic acid chlorides than it does with those of the aromatic series. Thus, reaction of isovaleryl chloride with dimethylaniline at high temperatures, without a catalyst, has been shown to result in formation of N-methylisovaleroanilide. Here one of the N-methyl groups has been replaced, but a substitution of the acyl group has also been effected in the ring.[871] Substitution of the acyl group in the nucleus, without derangement of the N-alkyl groups, has been reported in the presence of zinc chloride. Dimethylaniline with oenanthylic acid chloride thus gives *p*-dimethylaminooenanthophenone, $CH_3(CH_2)_5.CO.C_6H_4.N(CH_3)_2$, together with a compound of undetermined structure.[872]

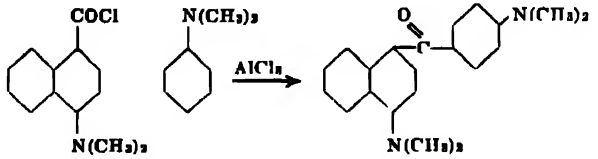
With aroyl chlorides, however, a similar condensation is difficult. Thus, in an attempt to react benzoyl chloride and dimethylaniline with anhydrous aluminum chloride in order to synthesize *p*-dimethylaminobenzophenone,[873] the condensation was effected, but the yield was very poor, probably because of further condensation of the ketone formed with unreacted dimethyl aniline. When benzanilideimido chloride was substituted for benzoyl chloride, however, and the condensation was carried out in carbon disulfide with anhydrous aluminum chloride at the ordinary temperature, a high yield of *p*-dimethylaminobenzophenone was obtained after 24 hours, the reaction proceeding:

[870] F. Krafft, *Ber.*, **23**, 2389-2393 (1890).
[871] V. Auger, *Compt. rend.*, **139**, 299-301 (1904); *C. Z.*, 1904, II, 703
[872] V. Auger, *Bull. soc. chim.* (*2*), **47**, 44 (1887).
[873] R. C. Shah and J. S. Chaubal, *J. Chem. Soc.*, 650-52 (1932).

$$C_6H_5C.(Cl):N.C_6H_5 + C_6H_5N(CH_3)_2 \xrightarrow{AlCl_3}$$
$$C_6H_5.C(:NC_6H_5).C_6H_4.N(CH_3)_2 \xrightarrow{H_2O}$$
$$C_6H_5.CO.C_6H_4.N(CH_3)_2 + NH_2C_6H_5$$

The condensation with benzanilideimido chloride has been extended also to substituted dialkyl anilines.[874]

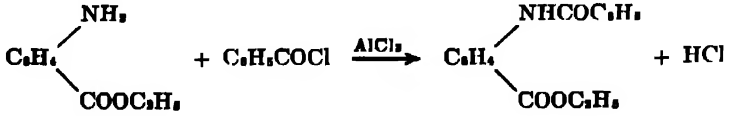
It is of interest, however, that in one instance a dialkyl aniline has been condensed with an acid chloride in the presence of aluminum chloride to give ring substitution in the *para*- position. Thus 4-dimethylamino-1-naphthoyl chloride and dimethylaniline treated cautiously under cooling with aluminum chloride give 4-(dimethylaminophenyl) 4'-(dimethylamino -1-naphthyl) ketone [875]:



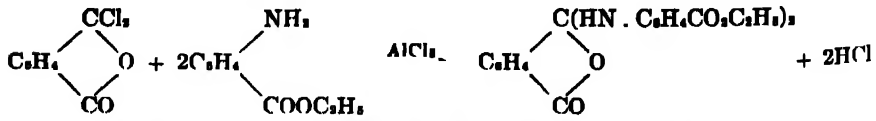
When like reaction was attempted with 1-(dimethylamino)naphthalene instead of dimethylaniline, however, only a tarry product was obtained

The Friedel-Crafts reaction, with anhydrous zinc chloride as catalyst, has been effectively used, in condensation of 2-naphthylamine with benzoyl chloride, with production of 1-benzoyl-2-benzamidonaphthalene in 30-40 per cent yield.[876] Similar treatment of 1-naphthylamine gives 1-benzamido-4-benzoylnaphthalene.[877] Substitution takes place at the nitrogen, as well as in the ring.

In aluminum chloride-catalyzed reaction of amino-substituted benzoates with benzoyl chloride or phthaloyl chloride, substitution of the acyl radical occurs for an N-hydrogen.[878] The reaction with the ethyl ester of *p*- or *m*-aminobenzoic acid and benzoyl chloride proceeds:



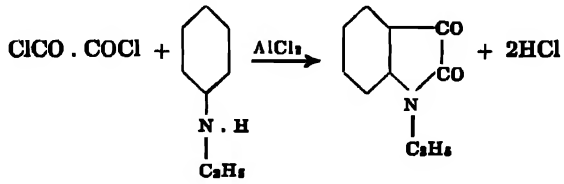
Phthaloyl chloride reacts as the lactone:



[874] R. C Shah and M B Ichaporia, *J Chem Soc*, 894-896 (1935); *C. A.*, 29, 6557.
[875] B Gokhle and F A Mason, *J Chem Soc*, 118-126 (1931)
[876] K. Dziewoński L Kwieciński, and L Sternbach, *Bull intern. acad polonaise, Classe sci math nat*, 1934, *A*, 329-337; *C A*, 29, 1084.
[877] K. Dziewoński and L Sternbach. *Rocz. Chem*, 13, 704-719 (1933); *Brit. Chem Abs -A*, (1934), 419
[878] H Limpricht, *Ann*, 303, 274-289 (1898).

Aluminum chloride has been found to be an effective catalyst for promoting condensation of oxalyl chloride with N-monoalkyl amines for the production of nitrogen ring compounds, the reaction probably proceeding through primary replacement of N-hydrogen by the COCOCl group, and subsequent aluminum chloride-catalyzed ring closure.

Ethylaniline has been condensed with oxalyl chloride and aluminum chloride in carbon disulfide solution to give N-ethylisatin (m.p. 95°), the reaction proceeding [879]:



Here ring closure is effected during the acylation. The method seems general for the production of N-substituted isatins from secondary amines.

However, in attempting to prepare phenylisatin, Stollé [880] reacted diphenylamine with oxalyl chloride in the presence of aluminum chloride. Instead of the expected product he obtained acridine carboxylic acid; the intermediate product probably was *o*-anilinobenzoylformyl chloride.

β-N-Ethylaminonaphthalene and oxalyl chloride with aluminum chloride give β-ethylnaphthindol-1,2-dione.[881]

The condensation of N-monoarylaminoanthraquinones with oxalyl chloride in the presence of aluminum chloride leads to formation of N-anthraquinonylisatins.[882] Here probably introduction of the COCOCl residue into the amino- nitrogen occurs, with subsequent ring closure to the N-aryl substituent. The acylation of N-monoarylaminoanthraquinones is not possible by the use of such acid chlorides as benzoyl chloride, acetyl chloride, and carbonyl chloride.

N-Anthraquinonylisatins result from the condensation of oxalyl chloride with 1-*p*-toluidinoanthraquinone, 1,5-di-*p*-toluidinoanthraquinone, and 1,5-bis-β-naphthylaminoanthraquinone.

Amides

N-Aryl acetamides easily react with acyl halides in the presence of aluminum chloride and carbon disulfide to give normal substitution products. Thus, acetanilide and acyl halides have been shown to react according to the equation:

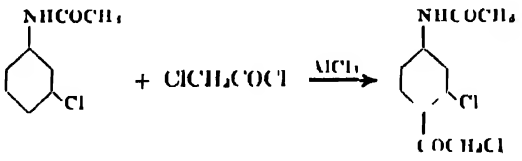
[879] R. Stollé, *Ber.*, **46**, 3915-3918 (1913); *C. A.*, **8**, 708; German P. 281,046 (1913) to R. Stollé, *C. A.*, **9**, 1999.
[880] R. Stollé, *J. prakt. Chem. (2)*, **105**, 137-148 (1922); *J. Chem. Soc. Abs.*, **124** (I), 1125 1127 (1923).
[881] Swiss P. 92,633, and 92,486-9 to H. Staudinger; *C. Z.*, 1923, II, 573.
[882] German P. 282,490 (1915) to Farbenfabrik vorm. F. Bayer & Co.; *J. Chem. Soc. Abs.*, **108** (I), 839 (1915); *C. Z.*, 1915, I, 852.

Kunckell [883] secured the following ketones from acetanilide and the indicated acyl halide:

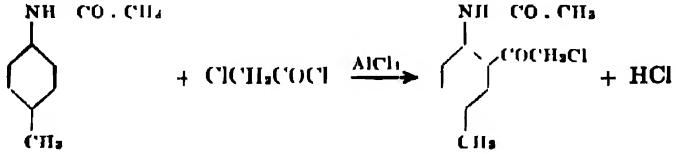
Acid halide	Ketone obtained	m.p. (°C.)
Acetyl bromide	*p*-acetylacetanilide	166–167
Propionyl chloride	*p*-propionylacetanilide	161
n-Butyryl chloride	*p*-*n*-butyrylacetanilide	142

The reaction proceeds even more easily with halogenated acyl halides He obtained an excellent yield of *p*-chloroacetylacetanilide, $Cl.CH_2.CO.C_6H_4.NH.COCH_3$ (m.p. 212°) from chloroacetyl chloride and acetanilide with carbon disulfide and aluminum chloride. Obviously the entering group goes *p*- to the acetamino group in the acylation of unsubstituted acetanilide.[884]

Similarly, with *m*-chloroacetanilide, chloroacetyl chloride yields *o*-chloro-*p*-acetylaminochloroacetophenone [885].



With aceto-*p*-toluidide, however, it was shown that the entering acyl group goes *ortho*- to the acetamino- group. The product obtained was *m*-methyl-*o*-acetylaminochloroacetophenone [886]



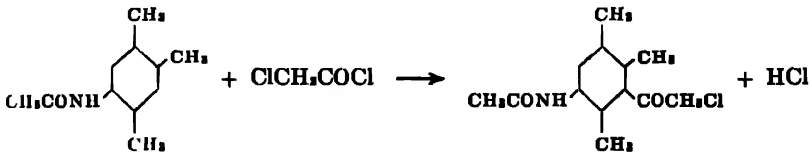
With aceto-*o*-toluidide and chloroacetyl chloride, the position of the entering acyl group could not be ascertained, except that it did not go *ortho*- to the acetamino- group. Since upon fusion with potassium hydroxide, acetanilides having a chloroacetyl group *ortho*- to the acetamino- group give indigo derivatives, *ortho*-substitution was hoped for Phenacetin also did not give *ortho*- substitution.[887]

A chlorine-substituted acetanilide was then reacted with chloroacetyl chloride.[888] Here the reaction proceeded,

[883] F. Kunckell, *Ber.*, 33, 2641-2644 (1900).
[884] F. Kunckell, *Ber.*, 33, 2644-2654 (1900); *cf.* German P. 105,199, *C. Z.*, 1900, I, 240
[885] F. Kunckell, *Ber. deut. pharm. Ges.*, 21, 419-456 (1911); *J. Chem. Soc., Abs.*, 100 I, 990 (1911)
[886] F. Kunckell, *Ber.*, 33, 2644-2654 (1900).
[887] F. Kunckell, *Ber.*, 34, 124-129 (1901).
[888] F. Kunckell and A. Richarts, *Ber.*, 40, 3394-3397 (1907).

with formation of 1-chloroacetyl-2-chloro-4-acetaminobenzene, m.p. 146-147°.

Asym-m-acetoxylidene and chloroacetyl chloride likewise did not give a compound in which the acyl group was *ortho-* to the acetamino-group.[889] Acetopseudocumidine entered into the following reaction:

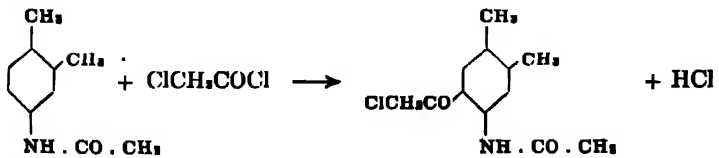


Here, too, the acyl group preferred not to go *ortho-* to the acetamino-group.

With α-bromopropionyl bromide and aceto-*o*-toluidide, two compounds, melting at 158° and 138°, were obtained. Their constitution could not be explained. Bromopropionyl bromide reacted normally with the acetoxylidine and the acetopseudocumidine, giving respectively:

α-bromopropionylacetoxylidine, m.p. 115-116°, and
α-bromopropionylacetopseudocumidine, m.p. 146°.

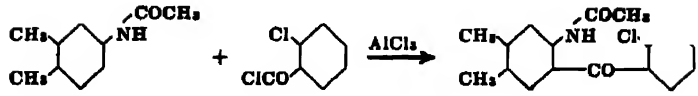
Later[890] Kunckell and Schneider reacted chloroacetyl chloride with 4-acetamino-1,2-dimethylbenzene and obtained *o*-substitution to the acetamino- group:



In this case the 2-methyl group has a *para-* directing influence, and the acetamino- group, an *ortho*-directing effect.

In following this same procedure, Kranzlein[891] obtained a 94 per cent yield of 4-acetamino-5-chloroacetyl-1,2-dimethylbenzene. Like reaction with *o*-chlorobenzoyl chloride instead of chloroacetyl chloride gave the expected 2'-chloro-4,5-dimethyl-2-acetaminobenzophenone, in 80 per cent yield:

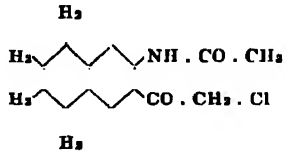
[889] F. Kunckell, *Ber.*, 33, 2644-2654 (1900).
[890] F. Kunckell and H. Schneider, *J. prakt. Chem.*, 86, 420-432 (1912); *C. A.*, I, 777.
[891] P. Kranzlein, *Ber.*, 70, 1776-1787 (1937).



Attempted ring closure of the above product was unsuccessful. Acid hydrolysis and subsequent treatment with sodium hydroxide resulted in formation of 2′-chloro-4,5-dimethyl-2-aminobenzophenone.

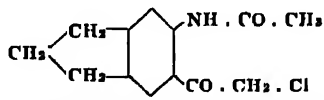
Kranzlein[891] expected that 2-acetamino-5,6,7,8-tetrahydronaphthalene and 5-acetaminohydrindene would behave in the same way, the cyclic methylene residues having the same influence as the two *o*-methyl groups in 4-acetamino-1,2-dimethylbenzene. The cyclic methylene residues were found to have the expected effect, and the following compounds were prepared:

(I)



2-acetamino-3-chloroacetyl-5,6,7,8-tetrahydronaphthalene (m.p. 148°) in 27 per cent yield.

(II)



5-acetamino-6-chloroacetylhydrindene, (m.p. 167°) in 52 per cent yield

Reaction of aceto-β-naphthylamide with oxalyl chloride and aluminum chloride in carbon disulfide results in formation of what probably is 2-acetaminoacenaphthene-quinone, m.p. 232°. Here the COCOCl residue of oxalyl chloride adds to the naphthylamide, with subsequent *peri*-ring closure.[892]

Acetanilide with thionyl chloride and aluminum chloride in carbon disulfide gives an 85 per cent yield of 4,4′-diacetaminodiphenyl sulfoxide.[893]

Compounds with Nitrogen in the Ring

Heterocyclic compounds of nitrogen are not easily acylated by the Friedel-Crafts reaction. Reported instances of acylation with pyrroles, carbazoles, quinolines, and pyrazoles are somewhat isolated cases, and reveal little in the way of generalities, except that here, as in the aromatic series, the presence of activating groups facilitates reaction.

Pyridine

Pyridine does not undergo Friedel-Crafts acylation. Pyridine and its salts, treated under very varied conditions with acetyl chloride or ben-

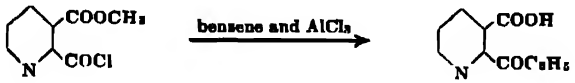
[891] G. Gallas and G. Bermúdez, *Anal. Fis. Quím.*, **29**, 464-469 (1931); *Brit. Chem. Abs.-A*, 1284 (1931).
[892] S. Sugasawa and K. Sakurai, *J. Pharm. Soc. Japan*, **60**, 23-4, *Abstracts* (in English 1-3 (1940); *C. A.*, **34**, 9704.

zoyl chloride in the presence of aluminum chloride do not give ketones. Although in some cases there is energetic evolution of hydrogen chloride, only tarry products result.[894] Since nitrobenzene also does not undergo Friedel-Crafts reactions, it has been suggested that similar electronic disturbances in nitrobenzene and in pyridine are responsible for their inactivity.[895]

In order to prepare pyridyl ketones, the chlorides of pyridine carboxylic acids have been reacted with aromatic hydrocarbons and with phenol ethers. Wolffenstein and Hartwich [894] have shown that the presence of thionyl chloride is necessary for condensation to occur. This may be provided by not completely purifying the acid chloride obtained by reaction of the carboxylic acid with thionyl chloride. Using such impure acid chlorides, these workers have prepared ketones from pyridine-α-carboxylic acid and benzene or anisole, from pyridine-β-carboxylic acid with the same components and with naphthalene, and from pyridine-α,β'- or α,α'-dicarboxylic acids and benzene. Aluminum chloride was used as catalyst. As an example, the condensation of pyridine-α-carboxylic acid chloride with benzene yields phenyl-α-pyridyl ketone:

Pyridine-β-carboxylic acid chloride has been similarly reacted with toluene and *m*-xylene.[896]

Mono-esters of pyridine dicarboxylic acid chlorides condense with benzene in the presence of aluminum chloride. Substitution of the halogen occurs, with simultaneous hydrolysis of the ester [897]:



The α-ester, β-chloride undergoes like condensation.

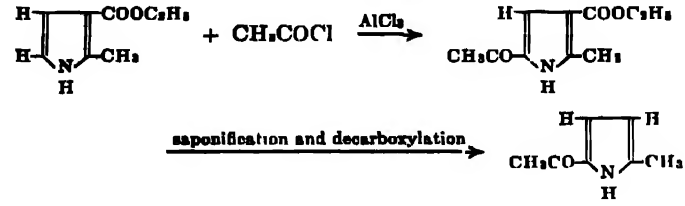
Pyrrole

It has been reported that by reacting acetyl chloride with pyrrole in ether, in the absence of catalyst, 2-acetylpyrrole is formed, together with N-acetylpyrrole.[898] Similar treatment of N-methylpyrrole gives 1.8 g of N-methyl-2-acetylpyrrole from 5 g of the pyrrole.[899]

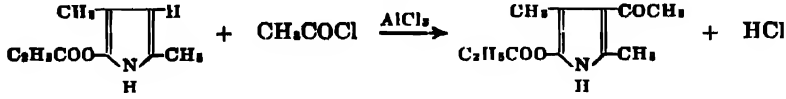
Grignard reagents and alkali-metal compounds of pyrrole have been more generally used in the preparation of pyrrole ketones, however; and until the recent investigations of Hans Fischer and co-workers aluminum chloride was not considered as a catalyst for acylations of this type. Fischer has shown that acyl derivatives of alkyl-substituted pyrroles may

[894] C. Engler and P. Rosumoff, *Ber.*, 24, 2527-2529 (1891); *J. Chem. Soc. Abs.*, 60 (II), 1503 (1891)
R. Wolffenstein and F. Hartwich, *Ber.*, 48, 2043-2049 (1915); *C. A.*, 10, 768
[895] N. V. Sidgwick, "Organic Chemistry of Nitrogen," p. 522-523, Oxford, Clarendon Press, 1937.
[896] O. Halla, *Monatsh.*, 32, 747-751 (1911); *J. Chem. Soc Abs.*, 100 (I), 1021 (1911).
[897] A. Kurpal, *Monatsh.*, 31, 295-299 (1910); *C. A.*, 4, 185.
[898] K. Hess, *Ber.*, 43, 1569-1574 (1915).
[899] B. Oddo, *Ber.*, 47, 2427-2433 (1914).

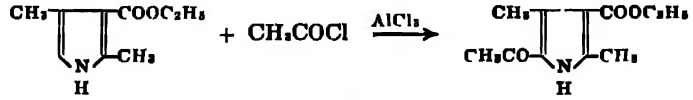
be prepared in almost quantitative yields by reaction of alkylated carbethoxy- pyrroles with acyl halides in the presence of aluminum chloride.[900] Treatment of 2-methyl-3-carbethoxypyrrole with acetyl chloride and aluminum chloride produces 5-acetyl-2-methyl-3-carbethoxypyrrole, subsequently decarboxylated to 2-methyl-5-acetylpyrrole.[901]



The condensation of 2,4-dimethyl-5-carbethoxypyrrole with acetyl chloride occurs according to the scheme [900]:

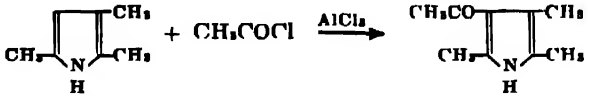


With 2,4-diethyl-5-carbethoxypyrrole, an 85 per cent yield of the ethyl ester of 2,4-diethyl-3-acetylpyrrole-5-carboxylic acid is thus obtained.[902] In the same manner, condensation of 2,4-dimethyl-3-carbethoxypyrrole

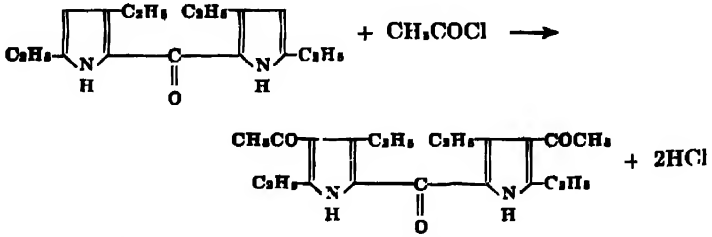


with acetyl chloride may be effected [900]: Propionyl chloride may be the acid chloride used.[903]

A trialkylated pyrrole undergoes easy Friedel-Crafts acylation [900]:

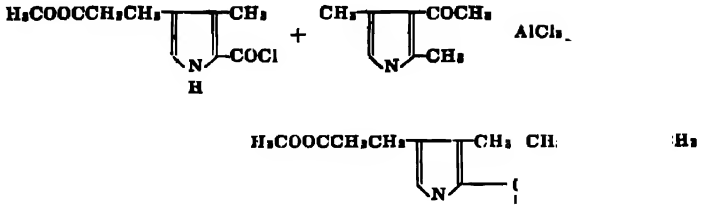


Similar condensation occurs with polyalkylated dipyrrole ketones [902]:



[900] H. Fischer and F. Schubert, *Z. physiol. Chem.*, 155, 99-112 (1926); *C. A.*, 21, 381
[901] H. Fischer, H Beyer, and E Zaucker, *Ann.*, 486, 55-70 (1931).
[902] H. Fischer and H. Orth, *Ann.*, 502, 237-264 (1933); *C. A.*, 27, 3471
[903] H. Fischer, M. Goldschmidt, and W. Nüssler, *Ann.*, 486, 1-54 (1931).

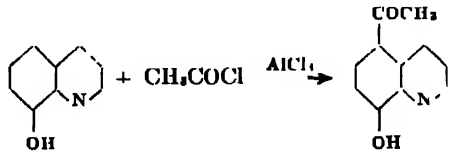
An acid chloride of the pyrrole series may be combined with an acylated pyrrole [902]:



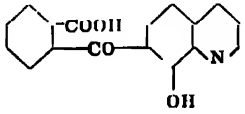
In reactions of this type, 2,4-dimethyl-3-carbethoxypyrrole or 2-methyl-3-carbethoxypyrrole may be used instead of the acetylated pyrrole. The fact that pyrrole ketones or esters undergo Friedel-Crafts acylation may indicate superaromatic properties of pyrroles.

Quinoline

Although quinoline and its derivatives have been reported not to undergo Friedel-Crafts acylation,[904] several reactions of this type are described in the literature. Using nitrobenzene as solvent, substantially in accordance with the process described by Behn,[905] and by Rosenmund and Schulz,[906] condensation of 8-hydroxyquinoline with acetyl chloride, chloroacetyl chloride, and benzoyl chloride is reported, with formation of the corresponding 5-acyl-8-hydroxyquinolines.[907] Reaction with acetyl chloride and aluminum chloride in nitrobenzene at 70° for twelve hours gives a 45 per cent yield of 5-acetyl-8-hydroxyquinoline:



With propionyl chloride, the corresponding propionyl derivative is secured. Interaction of one mole each of 8-hydroxyquinoline and phthaloyl chloride under like conditions gives 7-*o*-carboxybenzoyl-8-hydroxyquinoline,



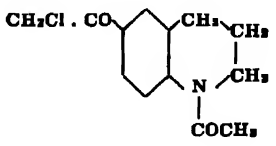
together with a small amount of α-8,8′-dihydroxydiquinonylphthalide as by-product. With two moles of 8-hydroxyquinoline and one mole of

[902] R. Wolffenstein and F. Hartwich, *Ber.*, 48, 2043-2049 (1915).
[904] German P. 95,901 (1897) to Richard Behn; *C. Z.*, 1898, I, 1223.
[905] K. W. Rosenmund, and H. Schuls, *Arch. Pharmaz. Ber. deut. pharm. Ges.*, 265, 308-319; *C. Z.*, 1927, I, 3184.
[907] K. Matsumura, *J. Am. Chem. Soc.*, 52, 4433-4436 (1930); *C. A.*, 25, 106.

phthaloyl chloride, another phthalide, 8,8'-dihydroxydiquinonyl phthalide, was formed. The positions of attachment of the two quinoline rings to the phthalic acid group could not be ascertained.[908]

8-Methoxyquinoline is acylated by reaction with chloroacetyl chloride in petroleum ether in the presence of aluminum chloride to give 8-methoxy-*x*-chloroacetylquinoline (m.p. 58°) in 80 per cent yield.[909]

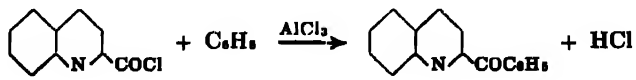
Friedel-Crafts acylation has also been shown to take place with 1-acetyl-1,2,3,4-tetrahydroquinoline and chloroacetyl chloride with aluminum chloride in carbon disulfide.[910] Substitution occurs in the benzene ring, the reaction product being 1-acetyl-6-chloroacetyl-1,2,3,4-tetrahydroquinoline, m.p. 137°:



Bromoacetyl bromide undergoes like reaction. Chloroacetyl chloride, bromoacetyl bromide and acetyl bromide were also shown to acylate 1-acetyl-6-methyl-1,2,3,4-tetrahydroquinoline in like manner, the entering acyl group going *ortho-* to the alkyl substituent. The reaction was found to occur also with 1-acetyl-8-methyl-1,2,3,4-tetrahydroquinoline and chloroacetyl chloride or bromoacetyl bromide.[911]

Benzanthronequinoline may be reacted with benzoyl chloride, chlorobenzoyl chloride, or nitrobenzoyl chloride and aluminum chloride to give ketones which are useful in the dyestuff industry.[912]

Aroyl derivatives of quinoline may be prepared by condensing quinoline acid chlorides with benzene in the presence of aluminum chloride. Thus, quinoline 2-carboxylic acid chloride yields 2-benzoylquinoline[913]:



Carbazole

Friedel-Crafts acylation of carbazole gives diacylation, even in the presence of a limited amount of acid halide[914]:

[908] K. Matsumura, *J. Am. Chem. Soc.*, 57, 124-128 (1935); *C. A.*, 29, 1424.
[909] S. Fränkel and O. Grauer, *Ber.*, 46, 2551-2554 (1913).
[910] F. Kunckell and E. Vollbaue, *Ber.*, 42, 3196-3199 (1909).
[911] F. Kunckell, *Ber. deut. Pharm. Ges.*, 20, 277-293 (1910); *C. Z.*, 1910, II, 861.
[912] Brit. P. 205,502 (1923); German P. 412,053 (1924) to Farb. vorm. Meister Lucius & Brüning; *C. Z.*, 1924, I, 710.
[913] E. Besthorn, *Ber.*, 41, 2001-2003 (1908).
[914] S. G. P. Plant, K. M. Rogers, and S. B. C. Williams, *J. Chem. Soc.* (1935), 741-44.

The acyl group also goes into the 3,6- positions in like reaction of N-alkyl derivatives. Thus 9-methylcarbazole with acetyl bromide and aluminum chloride in carbon disulfide solution gives 3,6-diacetyl-9-methylcarbazole.

Acylation of N-acylcarbazole proceeds differently, however. In reacting 9-acetylcarbazole with acetyl bromide and aluminum chloride in carbon disulfide, a diacetylated carbazole (m.p. 104°) has been obtained.[915] Hydrolysis of this product was reported to give 3-acetylcarbazole.

Later, it was claimed that this hydrolysis product was not 3-acetylcarbazole, as was originally assumed, but 2-acetylcarbazole, and that the product of the reaction of 9-acetylcarbazole with acetyl bromide and aluminum chloride was, in reality, 9,2-diacetylcarbazole.[916] This was subsequently confirmed by Plant and Williams.[917]

Benzoylation of 9-acetylcarbazole similarly gives 9-acetyl-2-benzoylcarbazole which upon hydrolysis yields 2-benzoylcarbazole. Like reaction with 9-benzoylcarbazole yields 2,9-dibenzoylcarbazole, which also gives 2-benzoylcarbazole upon hydrolysis.[914]

The production of 9,2-diacyl derivatives is unusual in that 9-acyl derivatives are isomerized into 3-acyl carbazoles by treatment with aluminum chloride. Thus addition of aluminum chloride to 9-benzoyl carbazole and gradual heating to 120° gives 3-benzoylcarbazole, which upon subsequent reaction with benzoyl chloride yields 3,6-dibenzoylcarbazole.[918] Since isomerization of 9-acyl is effected by aluminum chloride, it is singular that migration of the 9-acyl group does not occur during the Friedel-Crafts reaction.

The hydrogenated N-acylcarbazoles do not behave as do the unhydrogenated derivatives in Friedel-Crafts acylations. 9-Acetyltetrahydrocarbazole and acetyl bromide with aluminum chloride in carbon disulfide give the 7,9-diacetyl derivative.[919] On the other hand, 9-acetylhexahydrocarbazole and acetyl chloride under like conditions yield the 6,9-diacetyl derivative. Since the hexahydrocarbazole contains one fully reduced ring, it behaves more like a simple benzene derivative than do the other acyl carbazoles.[920]

The condensation of carbazole or its derivatives with chlorides of higher aliphatic acids has been patented.[921] Interaction of one mole of carbazole with one mole of stearoyl chloride in carbon disulfide is claimed to give the N-compound, which upon treatment with aluminum chloride is rearranged to form 3-stearoylcarbazole, m.p. 105-106°. 3-Lauroylcarbazole (m.p. 101-102°) is similarly obtained. The following 3,6-diacyl carbazoles are also reported:

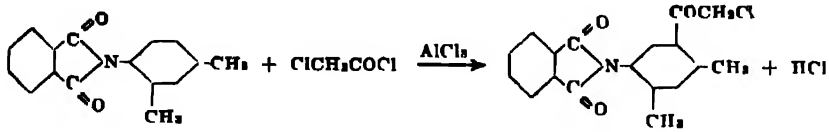
dilauroyl	m.p. 176°
dimyristyl	m.p. 169°
dipalmitoyl	m.p. 162°
distearoyl	m.p. 161–162°

[915] W. Borsche and M. Feise, *Ber.*, 40, 878-886 (1907).
[916] German P. 585,312 to I. G. Farbenindustrie; *C. Z.*, 1932, II, 2532.
[917] S. G. P. Plant and S. B. C. Williams, *J. Chem. Soc.* (1934), 1142-1143.
[918] S. G. P. Plant and M. L. Tomlinson, *J. Chem. Soc.* (1932), 2188-2192.
[919] S. G. P. Plant and K. M. Rogers, *J. Chem. Soc.* (1936), 40-1.
[920] D. R. Mitchell and S. G. P. Plant, *J. Chem. Soc.* (1936), 1295-1298.
[921] U. S. P. 2,101,859 (1937) to A. W. Ralston and C. W. Christensen (to Armour & Co.); *C. Z.*, 1938, I, 3112; Brit. P. 464,858 (1938) to Armour & Co., *C. A.*, 33, 2617; *Brit. Chem. Abs.*-B, (1939), 18.

The reaction of carbazole with carbamyl chloride for the preparation of carbazole dicarboxylic acid diamides has been claimed.[922] A molecular compound of the carbamyl chloride with aluminum chloride may be used, thus facilitating the reaction.

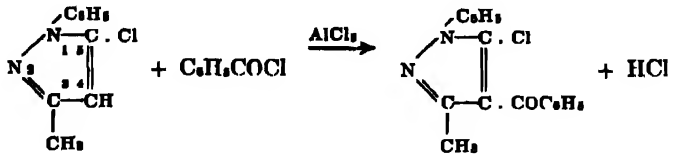
Phthalimides

N-Phenylphthalimides may undergo Friedel-Crafts acylation. Thus N-(2,4-dimethylphenyl)phthalimide with chloroacetyl chloride in the presence of aluminum chloride yields N-(2,4-dimethyl-5-chloroacetylphenyl)phthalimide.[923] Similar condensations, using zinc chloride as catalyst, have also been reported.[924]



Pyrazoles

N-Aroyl derivatives of various pyrazoles have been prepared by reaction with an aroyl halide in the absence of a catalyst. Replacement of C-hydrogen, however, is not easily effected. Aluminum chloride has been successfully used as catalyst in the production of 4-aroyl derivatives of 5-chloro-1-phenyl-3-methylpyrazole. The condensation is readily effected with benzoyl chloride and those derivatives of benzoyl chloride which do not contain strongly electronegative groups in the *meta-* or *para-* positions. Aliphatic acid chlorides do not undergo the reaction.[925] Condensation with benzoyl chloride proceeds:



Attempts to prepare 4-acyl derivatives of 5-chloro-3-methylpyrazole by this method led only to the formation of 1-acyl compounds. It was found that only those chloropyrazoles which have an aryl group in the 1-position yield ketones; however, the substituent in the 3-position may be an alkyl or aryl group. For example 1-tolyl-3-methyl-4-chloropyrazole gave a 90 per cent yield of the 4-phenyl ketone, whereas 1-methyl- and 1-ethylchloropyrazole gave no ketone. The 3-substituent, however, may be aromatic or aliphatic.

[922] U. S. P. 2,127,227 (1938) to H. Hopff and H. Ohlinger (to I. G.); *C. A.*, 33, 1759. Brit. P. 456,070 (1936) to I. G.; French P. 803,287 (1936) to I. G.; *Brit. Chem. Abs.*-B, 130 (1937); *C. A.*, 31, 3615.
[923] F. Bodmus, *Chem. Ztg.*, 40, 326 (1916); *C. Z.*, 1916, I, 1150.
[924] *cf.* G. Hanschke, *Ber.*, 42, 2021-2030 (1909). E. Froelich, *Ber.*, 17, 2673-2681; 17, 1801-1809 (1884).
[925] A. Michaelis and C. A. Rojahn, *Ber.*, 50, 757-753 (1917); *C. A.*, 11, 2261. For attempted reaction of 3,5-dimethylpyrazole with acetyl chloride, see E. Ochiai, *J. Pharm. Soc. Japan*, 60, 167-74 (German abstr., 55-7) (1940); *C. A.*, 34, 5449.

The synthesis could not be used with those pyrazolones which yield O- or O,N-substituents. Thus 1-phenyl-3-methyl-5-pyrazolone yielded the 5-O-benzoyl compound, and 3-methyl-5-pyrazolone gave the N^1, O^5-dibenzoate.[926]

Recently, however, Friedel-Crafts acylation of 1-phenyl-2,3-dimethyl-5-pyrazolone has been claimed.[927] Reaction with diethylacetyl chloride in the presence of aluminum chloride yields 1-phenyl-2,3-dimethyl-4-diethylacetyl-5-pyrazolone, m.p. 132°.

Acylation of Aromatic Compounds of Arsenic and of Selenium

An attempt has been made to react acyl halides in the presence of aluminum chloride with aryl arsines, but decomposition resulted, with liberation of arsenic trichloride. Phenyldichloroarsine thus gives with acetyl chloride a 52 per cent yield of acetophenone:

$$C_6H_5AsCl_2 + CH_3COCl \xrightarrow{AlCl_3} CH_3COC_6H_5 + AsCl_3$$

Like decomposition occurs when chloroacetyl chloride is the acid halide used. Nitrophenyldichloroarsine undergoes similar decomposition when acylation is attempted.[928]

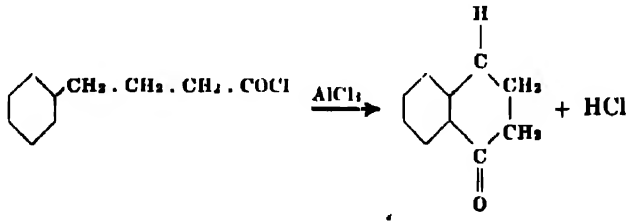
Aryl compounds of selenium may undergo normal Friedel-Crafts acylation. Selenonaphthene with acetyl chloride in carbon disulfide solution in the presence of aluminum chloride yields methyl selenonaphthyl ketone.[929]

[926] C. A. Rojahn, *Ber.*, **55**, 291-294 (1922).
[927] German P. 659,483 (1938) to H. P. Kaufmann; *C. A.*, **32**, 6009.
[928] M. S. Malinovskii, *J. Gen. Chem. (U. S. S. R.)*, **5**, 1355-1358 (1935); *C. A.*, **30**, 2182.
[929] G. Komppa and G. A. Nyman, *J. prakt. Chem.*, **19**, 229-236 (1934); *C. A.*, **28**, 2710.

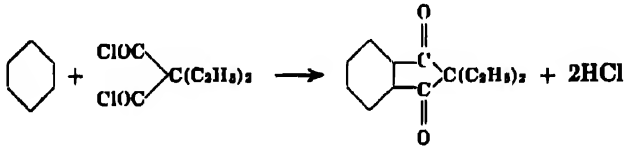
Chapter 7

Friedel-Crafts Synthesis. Part III. Ring Closure with Evolution of Hydrogen Chloride

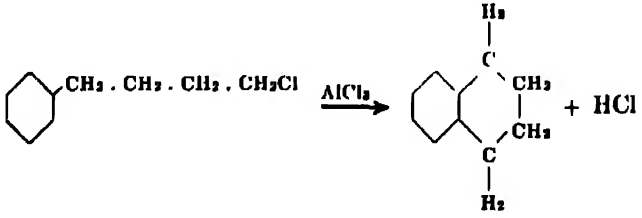
The use of aluminum chloride in effecting ring closure with certain halogenated organic compounds is a useful tool in the synthesis of polynuclear hydrocarbons. The condensation may be intramolecular,[1]



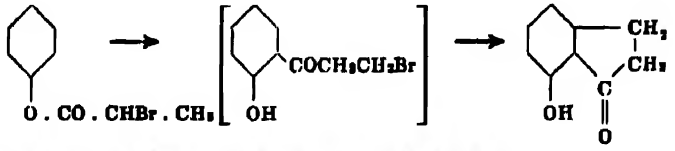
or intermolecular.[2]



Intramolecular condensations have been effected not only with numerous acyl halides but also with ω-halogenoalkyl benzenes[3]:

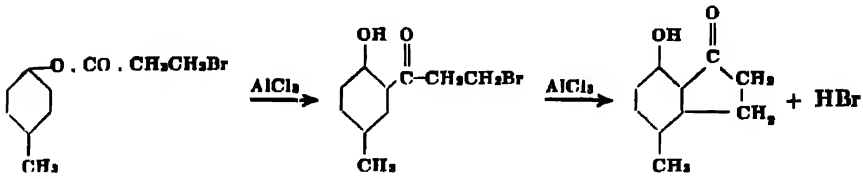


A halogenated ester may undergo ring closure,[4] probably with preliminary rearrangement to β-halogenated hydroxy- ketone:



[1] E. L. Martin and L. F. Fieser, *Organic Syntheses*, 15, 77-79 (1935).
[2] M. Freund and K. Fleischer, *Ann.*, 373, 291-336 (1910).
[3] J. v. Braun and H. Deutsch, *Ber.*, 45, 1267-1274 (1912).
[4] K. v. Auwers and E. Hilliger, *Ber.*, 49, 2410-2413 (1916).

Ring closure of aryl esters of β-chloropropionic acids have been shown to proceed with intermediate formation of hydroxy- ketones [5]:



Ring closure of α-halogenated aryl butyrates [6] is also effected with aluminum chloride.

The ketonic group has an activating influence on ring closure. With ketones, ring closure is effected even with certain aryl derivatives of acetyl chloride, but aralkyl halides with less than 3 carbon atoms do not undergo ring closure under the most stringent conditions, and good yields are obtained only with ω-halogenated butyl or amyl benzenes.[7]

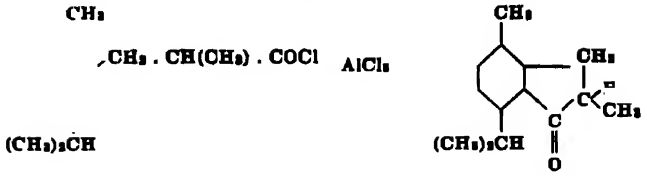
Table 18 has been compiled to illustrate the types of ring closures which have been effected by the action of aluminum chloride on acid halides. For convenience they have been classified as follows:

Polynuclear derivatives of acetyl halides
Cyclic derivatives of propionyl, isobutyryl, butyryl, and valeryl halides
Aralkyl dicarboxylic acid halides
Derivatives of benzoyl chloride
Alkoxy- or aryloxy- derivatives of the foregoing acid halides

Ring closure of compounds of nitrogen, sulfur, or arsenic * and ring closures effected through intermolecular condensations † are listed elsewhere.

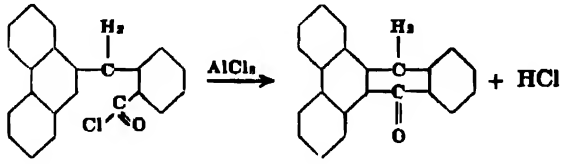
Naphthylacetyl halides yield acenaphthenones. Aryl derivatives of propionyl chloride generally give hydrindones, whereas tetrahydronaphthalenes are produced from arylbutyryl chlorides. Although the formation of a seven-membered ring from phenylvaleryl chloride has been cited,[8] aryl derivatives of valeryl chloride generally give tetrahydronaphthalenes. Branched chains give rings corresponding to the number of carbon atoms in the straight chain. Thus cymylisobutyryl chloride gives the corresponding hydrindone and not the tetrahydronaphthane [9]:

[5] F. Mayer and L. van Zutphen, *Ber.*, **57**, 200-202 (1924). F. Krollpfeiffer and H. Schultze, *Ber.*, **57**, 600-601 (1924).
[6] K. v. Auwers, *Ann.*, **439**, 132-175 (1924).
[7] J. v. Braun and H. Deutsch, *loc. cit.*; J. v. Braun and M. Kuhn, *Ber.*, **60**, 2557-2566 (1927).
* See pages 412-427.
† See page 427.
[8] F. S. Kipping and A. E. Hunter, *J. Chem. Soc.*, **79**, 602 (1901).
[9] W. G. Whittleston, *J. Am. Chem. Soc.*, **59**, 825-826 (1937).

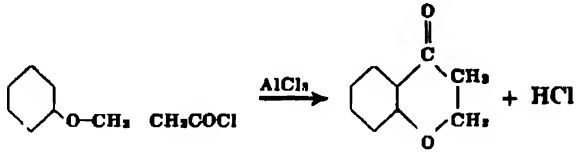


In general, branching of the ring increases the yield of the cyclic compound formed from this chain. Nuclear alkylation of the aromatic residue likewise favors ring formation.[10]

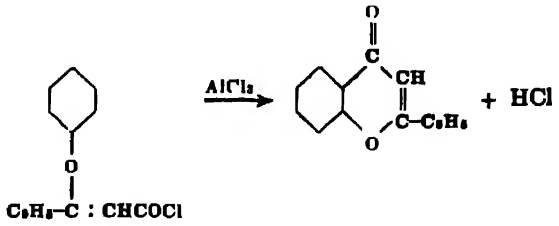
Aralkyl derivatives of benzoyl chloride may undergo ring closure with replacement of an adjacent labile hydrogen. Thus *o*-9-phenanthrylmethylbenzoyl chloride yields a benzanthrone[11]:



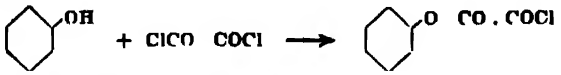
Ring closure of aralkyl acid halides having an ether linkage in a 3- or 4-carbon chain leads to formation of ring compounds of oxygen[12]:



The method gives theoretical yields of flavones from β-aryloxycinnamoyl chlorides[13]:

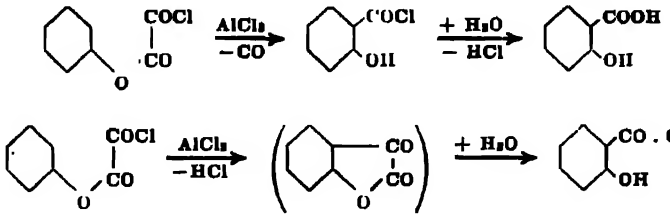


Oxalyl chloride reacts easily with phenols to give mono-esters. With phenol, for example, the reaction is

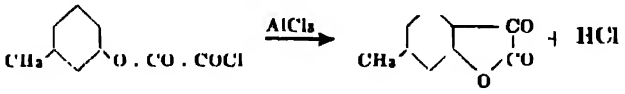


[10] F. Mayer and G. Stamm, *Ber.*, 56, 1424-1433 (1923).
[11] E. Bergmann and T. Berlin, *J. Chem. Soc.*, 488-494 (1939).
[12] F. Arndt and G. Kallner, *Ber.*, 57, 202-206 (1924).
[13] S. Ruhemann, *Ber.*, 46, 2188-2197 (1913).

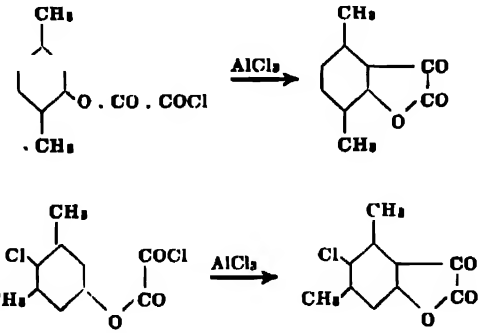
Under the influence of aluminum chloride in carbon disulfide solution, the phenyl oxalyl chloride formed is changed to give salicylic acid and a little (*o*-hydroxyphenyl)glyoxylic acid.[14] The reactions may proceed:



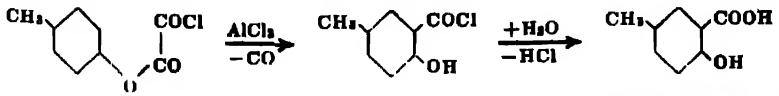
With *m*-tolyl oxalyl chloride, however, the following occurs:



Whether a cumarondione or a hydroxy- carboxylic acid (*e.g.*, salicylic acid) is formed by the action of aluminum chloride on an aryl oxalyl chloride depends upon the stability of the cumarandione. The stability of cumarandiones has been shown to be increased by the presence of substituents in the *meta*- position, but diminished by those in the *ortho*- or *para*- positions. Thus *p*-tolyl oxalyl chloride gives mainly *p*-cresotic acid, which is analogous to the result obtained with phenyl oxalyl chloride. Besides *meta*-tolyl oxalyl chloride, other aryl oxalyl chlorides having a *meta*-substituent have been converted to cumarandiones:



However, in the case of *p*-tolyl oxalyl chloride, the following occurs:



(Text continued on p. 412)

[14] R. Stolle, *Ber.*, **47**, 1130-1132 (1914). R. Stolle and E. Knebel, *Ber.*, **54**, 1213-1220 (1921); *J. Chem. Soc. Abs.*, **120** (I), 878.

Table 18.

Polynuclear Derivatives of Acetyl Halides

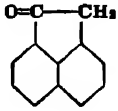
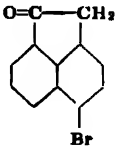
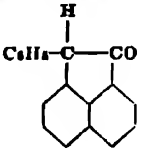
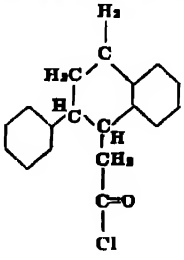
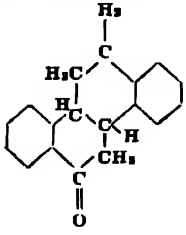
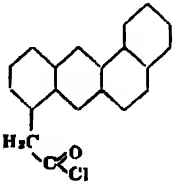
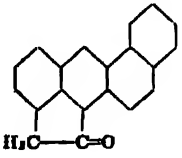
Acid Chloride	Product	Yield	Ref.
α-naphthylacetyl chloride or bromide	acenaphthenone 		21
4-bromonaphthyl-1-acetyl chloride	3-bromo-7-acenaphthenone 		8
phenyl-α-naphthyl acetyl chloride	7-phenylacenaphthenone (16 g from 25 g acid) 		22
cis-2-phenyl-1,2,3,4-tetrahydro-1-naphthalene-acetyl chloride 	*cis*-6-keto-5,6,11,12,13,14-hexahydrochrysene 	81%	5
1,2-benzanthracene-8-acetyl chloride 	1-ketocholanthrene 	72%	50

Table 18—*(Continued)*

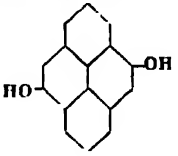
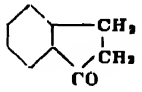
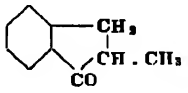
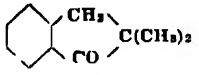
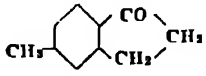
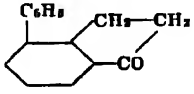
Acid Chloride	Product	Yield	Ref.
biphenyl-*o*-*o'*-diacetyl chloride	1,6-dihydroxyprene 		20
	Cyclic Derivatives of Propionyl Halides		
β-phenylpropionyl chloride	1-hydrindone 	55–95%	2,3,13, 14,26
β-phenyl-α-methyl-propionyl chloride	2-methyl-1-hydrindone 	70–80%	16
β-phenyl-α,α-dimethyl-propionyl chloride	2,2-dimethyl-1-hydrindone 	80%	
β-phenyl-α,α-diethyl-propionyl chloride	2,2-diethyl-1-hydrindone		1
isopropylbromophenyl-propionyl chlorides	isopropylbromohydrindones	64–82%	12
α-phenyl-β-phenyl-propionyl chloride	2-phenyl-1-hydrindone		53
β-*m*-tolylpropionyl chloride	5-methyl-1-hydrindone 		54
β-(*o*-chlorophenyl)-propionyl chloride	4-chloro-1-hydrindone	93%	46
2-β-diphenylpropionyl chloride	4-phenyl-1-hydrindone 		38
methylbromophenylpropionyl chloride	4-methyl-7-bromohydrindone-1 (I) and 7-methyl-4-bromo-hydrindone-1 (II)		11

Table 18—*(Continued)*

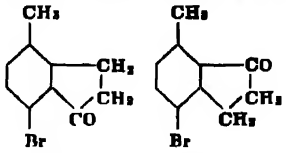
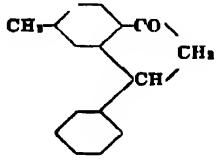
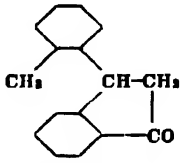
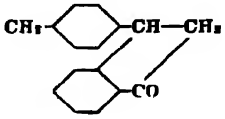
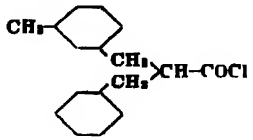
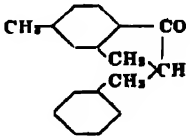
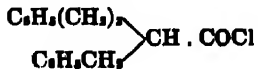
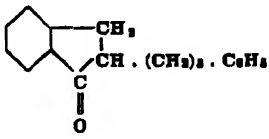
Acid Chloride	Product	Yield	Ref
	(23 g of I and 42 g of II from 78 g of the chloride mixture)  (I) (II)		
β-*m*-tolyl-β-phenylpropionyl chloride	5-methyl-3-phenylhydrindone-1 	60%	54
β-*o*-tolyl-β-phenylpropionyl chloride	3-*o*-tolyl-1-hydrindone 	80%	54
β-*p*-tolyl-β-phenylpropionyl chloride	3-*p*-tolyl-1-hydrindone 	70%	54
α-benzyl-β-(*m*-tolyl)-propionyl chloride 	2-benzyl-5-methylhydrindone 	75%	54
benzyl-γ-phenylpropyl-acetyl chloride 	2-γ-phenylpropylhydrindone 	60%	38

Table 18—*(Continued)*

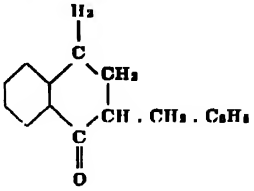
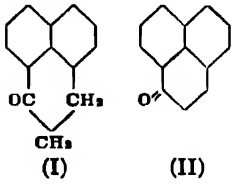
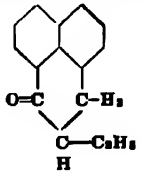
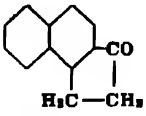
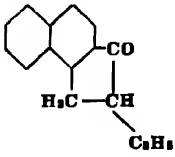
Acid Chloride	Product	Yield	Ref.
(β-phenylethyl)-benzylacetyl chloride	β-benzyl-α-tetralone 	60%	36
β-(naphthyl-1)-propionyl chloride	7,8-dihydro-9-phenalone (I) or 9-phenalone (II) (1.4 g of (I) from 4.5 g of chloride)  (I) (II)		(I) 8 (II) 51
β-(naphthyl-1)-α-ethylpropionyl chloride	8-ethyl-(7,8-dihydro-9-phenalone) (19.5 g from 20 g chloride) 		8
β-(naphthyl-2)-propionyl chloride	4,5-benzo-indanone-1 	very low	8
β-(naphthyl-2)-α-ethyl-propionyl chloride	2-ethyl-(4,5-benzo-indanone-1) 		8
β-(4-bromonaphthyl-1)-propionyl chloride	7,8-dihydro-9-phenalone (0.9 g from 15 g of the chloride)		8

Table 18—*(Continued)*

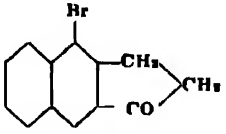
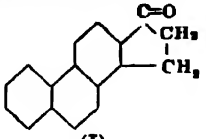
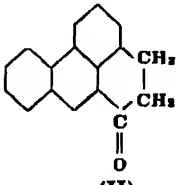
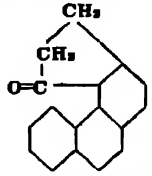
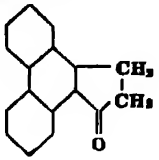
Acid Chloride	Product	Yield	Ref.
β-(1-bromonaphthyl-2)-propionyl chloride	4-bromo-(5,6-benzoindanone-1) 	low	8
β-(1-phenanthryl)-propionyl chloride	3′-keto-1,2-cyclopentano-phenanthrene (I) and 5,6-benzo-1,2-dihydro-3-benzonaphthenone (II)  (I)  (II)	(I) 4% (II) 25%	6
β-(2-phenanthryl)-propionyl chloride	1′-keto-1,2-cyclopentano-phenanthrene (0.5 g from 1.0 g of acid)		6
β-(3-phenanthryl)-propionyl chloride	3′-keto-3,4-cyclopentano-phenanthrene 	74%	6
β-(10-phenanthryl)-propionyl chloride	1-keto-9,10-cyclopentano-phenanthrene (I) and 5,6-benzo-2,3-dihydro-1-benzonaphthenone (II) (1.81 g of mixture from 2.4 g of the acid) (I) 		6

Table 18—*(Continued)*

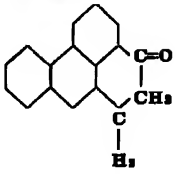
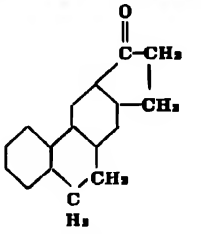
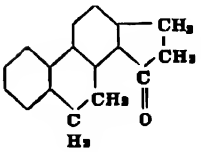
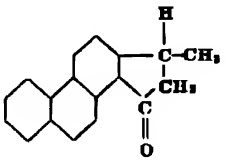
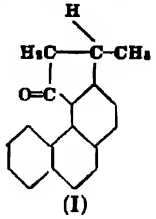
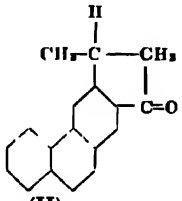
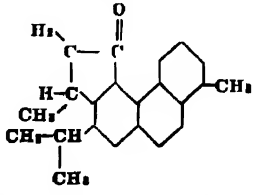
Acid Chloride	Product	Yield	Ref.
	(II) 		
-[2-(9,10-dihydrophen-anthryl)]-propionyl chloride	3'-keto-9,10-dihydro-2,3-cyclo-pentanophenanthrene (I) and 1'-keto-9,10-dihydro-1,2-cyclo-pentanophenanthrene (II) [(I) : 5.6 g from 10 g of acid. (II) : 1.2 g from 10 g of acid.]	97% of crude ketones	48
	 (I)		
	 (II)		
β-phenyl-β-(9-anthron-10-yl)-propionyl chloride	3-(9-anthron-10-yl)-1-hydrindone		56
β-(4-nitrophenyl)-β-(9-anthron-10-yl)-propionyl chloride	no reaction with $AlCl_3$ in CS_2 (due to nitro group)		55
Cyclic Derivatives of Isobutyryl Halides			
cymylisobutyryl chloride (β-cymyl-α-methyl propionyl chloride)	2,4-dimethyl-7-isopropyl-hydrindone (15 g from 20 g of acid)		28
β-(2-phenanthryl)-isobutyryl chloride	3-methyl-6,7-(1,2-naphtho)-hydrindone-1		43
			

Table 18—*(Continued)*

Acid Chloride	Product	Yield	Ref
β-(3-phenanthryl)-isobutyryl chloride	3-methyl-6,7-(7′,8′-naphtho)-hydrindone-1 (I) and 3-methyl-5,6-(1′,2′-naphtho)-hydrindone-1 (II) (3.8 g of I and 0.4 g of II from 14.2 g of acid)  (I)  (II)		42
β-6-retylisobutyryl chloride	1′-keto-3′-methyl-5,6-cyclopentanoretene 		47

Cyclic Derivatives of Butyryl Halides

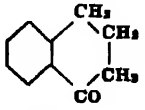
γ-phenylbutyryl chloride	α-keto-1,2,3,4-tetrahydronaphthalene	10% 70% 74–91%	3,14,15,17 27 29
			
γ-phenyl-α-methyl-*n*-butyryl chloride	2-methyl-1-keto-1,2,3,4-tetrahydronaphthalene	70%	15
γ-phenyl-γ-methyl-*n*-butyryl chloride	4-methyl-1-keto-1,2,3,4-tetrahydronaphthalene	70%	15
γ-phenyl-α,β-dimethyl-butyryl chloride	2,3-dimethyl-1-keto-1,2,3,4-tetrahydronaphthalene		52

Table 18—*(Continued)*

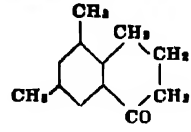
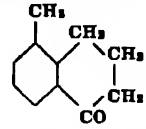
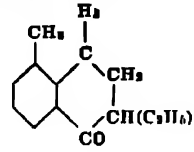
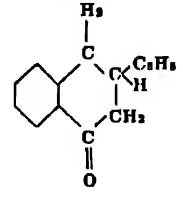
Acid Chloride	Product	Yield	Ref.
γ-(2,4-dimethylphenyl)-butyryl chloride	5-keto-1,3-dimethyl-5,6,7,8-tetrahydronaphthalene (13 g from 17 g $AlCl_3$) 		7
γ-*o*-tolylbutyryl chloride	5-keto-1-methyl-5,6,7,8-tetrahydronaphthalene (5 g from 7.5 g of acid chloride) 		9,10
γ-*p*-tolyl-*n*-butyryl chloride	7-methyl-1-keto-1,2,3,4-tetrahydronaphthalene	72%	15
γ-*p*-tolyl-α-methyl-*n*-butyryl chloride	2,7-dimethyl-1-keto-1,2,3,4-tetrahydronaphthalene	75% 92.5%	15 52
γ-*p*-tolyl-β-methyl-*n*-butyryl chloride	3,7-dimethyl-1-keto-1,2,3,4-tetrahydronaphthalene	72% 90%	15 52
γ-*p*-tolyl-γ-methyl-butyryl chloride	4,7-dimethyl-1-keto-1,2,3,4-tetrahydronaphthalene	76%	15
α,β-dimethyl-γ-(*o*-tolyl)-butyryl chloride	2,3,5-trimethyl-1-keto-1,2,3,4-tetrahydronaphthalene		52
α,β-dimethyl-γ-(*p*-tolyl)-butyryl chloride	2,3,6-trimethyl-4-keto-1,2,3,4-tetrahydronaphthalene		52
γ-*o*-tolyl-β-ethylbutyryl chloride	5-keto-1-methyl-7-ethyl-5,6,7,8-tetrahydronaphthalene		10
γ-*o*-tolyl-α-ethylbutyryl chloride	5-keto-1-methyl-6-ethyl-5,6,7,8-tetrahydronaphthalene (8 g from 9 g of acid chloride) 		10
β-γ-diphenylbutyryl chloride	3-phenyltetralone-1 	75%	38

Table 15—*(Continued)*

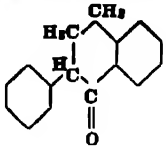
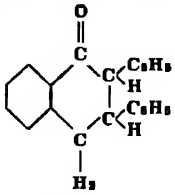
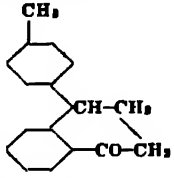
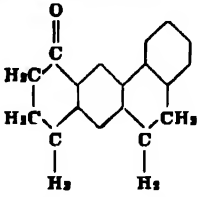
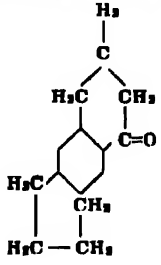
Acid Chloride	Product	Yield	Ref.
α,γ-diphenylbutyrylchloride	1-keto-2-phenyl-1,2,3,4-tetrahydronaphthalene 	94%	5
α,β,γ-triphenylbutyryl chloride	1-keto-2,3-diphenyl-1,2,3,4-tetrahydronaphthalene 	58%	4
γ,γ′-phenyl-*p*-tolyl-butyryl chloride	4-*p*-tolyl-1-keto-1,2,3,4-tetrahydronaphthalene 	70%	54
γ-(9,10-dihydro-2-phenanthryl)-butyryl chloride	8-keto-3,4,5,6,7,8-hexahydro-1,2-benzanthracene 	63%	49
γ-5-hydrindylbutyryl chloride	6,7-cyclopentano-1-tetralone 	92%	31

Table 18—*(Continued)*

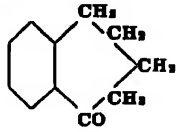
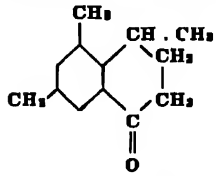
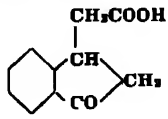
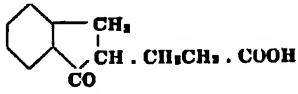
Acid Chloride	Product	Yield	Ref.
	Cyclic Derivatives of Valeryl Halides		
phenylvaleryl chloride	benzo-α-ketoheptamethylene 		14
γ-*p*-tolylvaleryl chloride	1,6-dimethyl-4-keto-1,2,3,4-tetrahydronaphthalene		52
γ-*o*-tolylvaleryl chloride	4,5-dimethyl-1-tetralone (8 g from 9.9 g of the acid)		9
γ-(2,5-dimethylphenyl)-valeryl chloride	1,4,5-trimethyl-8-keto-5,6,7,8-tetrahydronaphthalene		52
γ-(2,3-dimethylphenyl)-valeryl chloride	5-keto-1,3,8-trimethyl-5,6,7,8-tetrahydronaphthalene (20 g from 29 g of the chloride) 		7
β-methyl-γ-(*p*-tolyl)-valeryl chloride	1,2,6-trimethyl-4-keto-1,2,3,4-tetrahydronaphthalene		52
β-methyl-γ-(*o*-tolyl)-valeryl chloride	1,2,8-trimethyl-4-keto-1,2,3,4-tetrahydronaphthalene (8.3 g from 10.7 g of acid)		52
	Aralkyl Dicarboxylic Acid Halides		
β-phenylglutaryl chloride	3-ketohydrindyl-1-acetic acid 	80%	33
	(178 g from 208 g of chloride)		44
α-benzylglutaryl chloride	2-α-hydrindonyl-β-propionic acid 	30%	38

Table 18—*(Continued)*

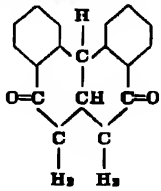
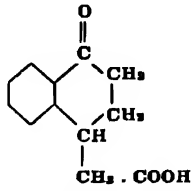
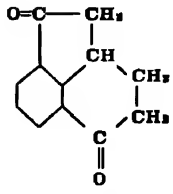
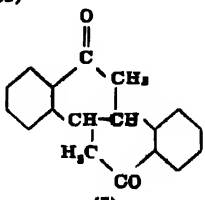
Acid Chloride	Product	Yield	Ref
β-benzohydrylglutaryl chloride	2,9-diketo-1,2,9,10,11,12-hexahydro-3,4-bensphenanthrene 	51.7%	32
di-*p*-tolyladipyl chloride	2,11-diketo-5,14-dimethyl-1,2,9,10,11,18-hexahydrochrysene		34
β-phenyladipyl chloride	1-keto-1,2,3,4-tetrahydronaphthalene-4-acetic acid (I) and	Less II than I	33
	3,7-diketo-1,2,3,4-tetrahydroacenaphthene (II)  (I)  (II)	Equal yield of I and II	44
β,β′-diphenyladipyl chloride	diketohexahydrochrysene (I) and	(I) 45%	45
	1-keto-3-phenyl-1,2,3,4-tetrahydronaphthalene-4-acetic acid (II)  (I)	(II) 8%	

Table 18—*(Continued)*

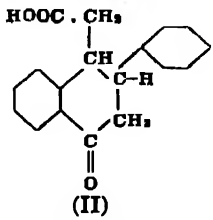
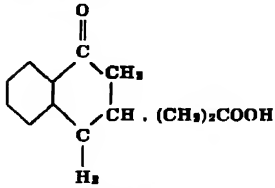
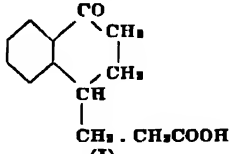
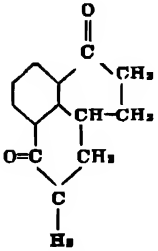
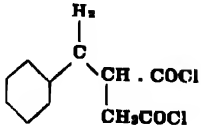
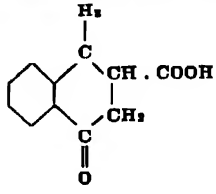
Acid Chloride	Product	Yield	Ref.
	 (II)		
β-benzyladipyl chloride	1-keto-1,2,3,4-tetrahydro-naphthalene-3-γ-propionic acid 	55%	37
γ-phenylpimelic acid chloride	1-keto-1,2,3,4-tetrahydro-naphthalene-4-γ-propionic acid (I) and	I : 53% II : 6%	44
	hexahydrobenznaphthene-α, α′-dione (II)  (I)  (II)	I : 17% II : 45%	33
benzylsuccinyl chloride 	1-keto-1,2,3,4-tetrahydro-naphthalene-3-acetic acid 	60–65%	36

Table 18—*(Continued)*

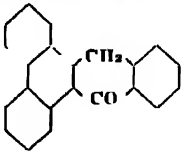
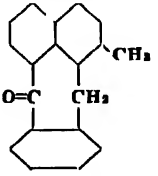
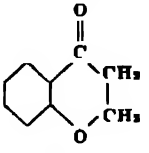
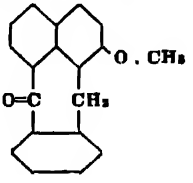
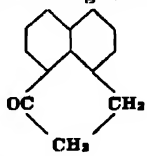
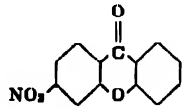
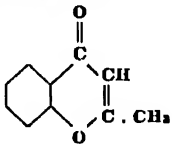
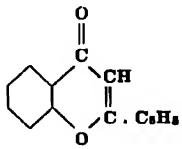
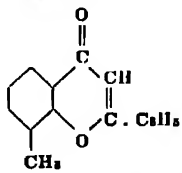
Acid Chloride	Product	Yield	Ref
α-truxillyl chloride (2,4-diphenylcyclobutone-1-dicarboxylic acid chloride)	α-truxone		35
	Aralkyl Derivatives of Benzoyl Chloride		
o-9-phenanthrylmethylbenzoyl chloride	1,2,3,4-dibenz-9-anthrone (2 g from 9 g of acid) 		19
2′-methyl-1′-naphthylmethyl-2-benzoyl chloride	1-methyl-7-pleiadenone 	75–85%	40
2′,3′, or 2′,6′- or 2′,7′-dimethyl-1′-naphthylmethyl-2-benzoyl chlorides	1,2- or 1,5- or 1,6-dimethyl-7-pleiadenone	75–85%	40
	Alkoxy or Aryloxy Derivatives of Acid Halides		
α-methyl-(p-methoxy-β-phenyl)-propionyl chloride	2-methyl-6-methoxyhydrindone		53
β-phenoxypropionyl chloride	chromanone	33%	39
	(8 g from 10 g of acid) 		23
β-p-cresoxy-propionyl chloride	6-methylchromanone	44%	39
2′-methoxy-1′-naphthyl-methyl-2-benzoyl chloride	1-methoxy-7-pleiadone 	75–85%	40

Table 18—*(Continued)*

Acid Chloride	Product	Yield	Ref.
β-(4-methoxynaphthyl-1)-propionyl chloride	7,8-dihydro-9-phenalone (3 mg from 16 g of chloride) 		8
5-nitrodiphenylether-2-carboxylic acid chloride	3-nitroxanthone 		7
β-phenoxycrotonyl chloride	2-methylchromone 		25
β-*p*-tolyloxycrotonyl chloride	2,6-dimethylchromone		25
β-phenoxycinnamoyl chloride	flavone 	almost theoretical	24
β-*m*-tolyloxycinnamoyl chloride	mixture of 5- and 7-methylflavones		24
β-*p*-tolyloxycinnamoyl chloride	6-methylflavone		24
β-*o*-tolyloxycinnamoyl chloride	8-methylflavone 		24
β-thymoxycinnamoyl chloride	5-methyl-8-isopropylflavone		24
β-*o*-methoxyphenoxycinnamoyl chloride	8-methoxyflavone		24

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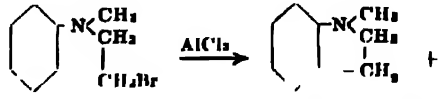
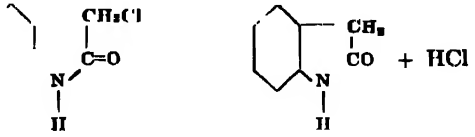
Intramolecular Ring Closure of Halogenated Nitrogenous Compounds

Cyclization of nitrogeneous acid halides in the presence of aluminum chloride may be used for the production of oxindoles, acridones, tetrahydroisoquinolines, isatins, azafluorenones, and azanthranols. ω-Halogeno-N-alkyl aryl amines do not easily undergo ring closure, although the conversion of N-ω-bromoethyl-N-ethyl aniline to N-methyldihydroindole in 35 per cent yield has been reported[15]:

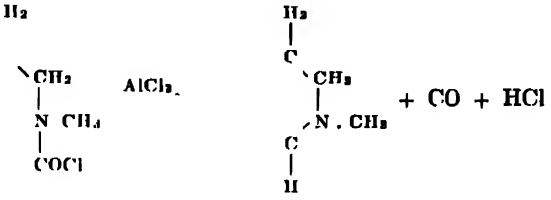


[15] J. v. Braun, K. Heider, and E. Muller, *Ber.*, 50, 1637-1651 (1917); *J. Chem. Soc. Abs.*, 114, 107 (1918).

Cyclization of N-chloroacetylarylamines with aluminum chloride occurs readily, an 85 per cent yield of oxindole being secured from chloroacetanilide:



The condensation is likewise applicable to homologs of chloroacetanilide.[16] It is not as applicable to aryl derivatives of glycyl chloride. Although N-β-phenylethyl-N-methylglycyl chloride gives a 40 per cent yield of N-methyltetrahydroisoquinoline,[17] the condensation is not gen-

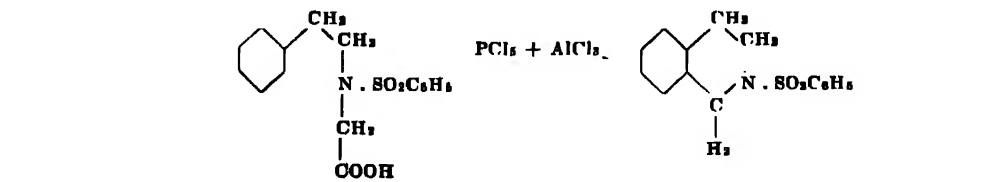


eral for N-aralkyl derivatives of glycine. Thus, N-methyl-N-benzyl glycyl chloride is decomposed by aluminum chloride, and no cyclization occurs[18]:

$$C_6H_5CH_2 . N(CH_3) . CH_2COCl \qquad C_6H_5CH_2 . N(CH_3) . CH_2Cl + CO$$

The easily hydrolyzed chloro- base decomposes further upon contact with water.

The cyclization of aralkyl glycyl chlorides may readily be effected by first introducing an arylsulfonyl residue into the nitrogen and then treating with aluminum chloride to effect ring closure:

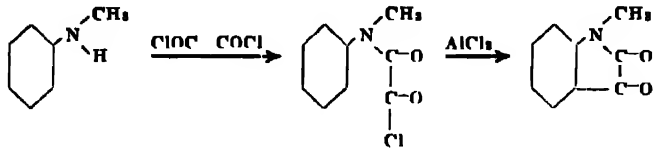


The benzenesulfonyl group is easily removed by acid hydrolysis. An 80 per cent yield of tetrahydroisoquinoline is secured.[19] The method is

[16] R. Stollé, R. Bergdoll, M. Luther, A. Auerhahn, and W. Wacker, *J. prakt. Chem.*, **128**, 1-43 (1930); *C. Z.*, 1930, II, 3408-3410.
[17] J. v. Braun and K. Wirz, *Ber.*, **60**, 102-110 (1927).
[18] C. Mannich and R. Kuphal, *Ber.*, **45**, 314-322 (1912).

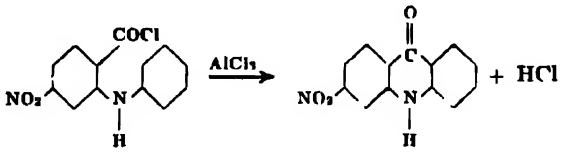
of general applicability for effecting ring closure of aralkyl glycyl chlorides.

Isatins may be produced by cyclizing the reaction products of aryl amines and oxalyl chloride [16]:

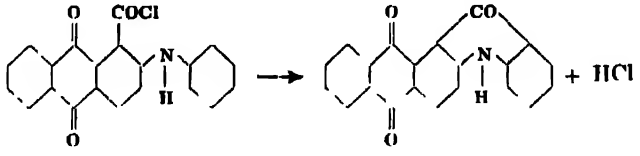


The method is rather general for the production of N-substituted isatins from secondary amines, although cyclization of the condensation product of diphenylamine and oxalyl chloride has been found to result in the production of acridine carboxylic acid.[20] It has also been extended to the preparation of naphthisatins in which the N-hydrogen is not replaced.[21]

Carboxylic acid chlorides of diphenylamino or of other N-aryl aminopolynuclear hydrocarbons may be cyclized to give acridones. Thus 5-nitrodiphenylamine-2-carboxylic acid chloride gives 2-nitroacridone [22]



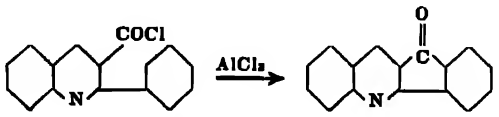
The cyclization finds application in the dyestuffs industry for the production of anthraquinone acridones [23]:



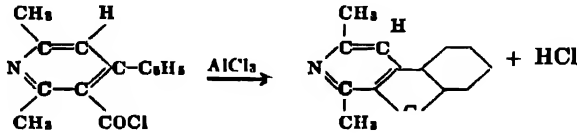
Carboxylic acid chlorides of arylated ring compounds of nitrogen may undergo ring closure by treatment with aluminum chloride. The reaction is generally applicable to compounds of the quinoline series. Thus

[19] J. v. Braun, G Blessing, and R. S. Cahn, *Ber*, 57, 908-912 (1924).
[20] R. Stollé, *J. prakt. Chem*, 105 (II), 137-148 (1922), *J Chem Soc. Abs*, 124 (I), 1125 (1923)
[21] British P. 230,358 (1926) and German P 446,946 to I G ; *C Z.*, 1927, II, 2228
[22] F. Ullmann and C. Wagner, *Ann.*, 355, 350-371 (1907)
[23] F Ullmann and M Rone, *Ann*, 380, 336-341 (1911)

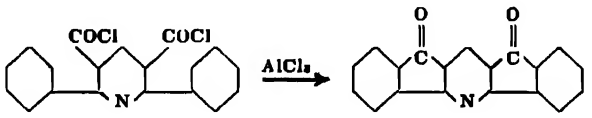
2-phenylquinoline-3-carboxylic acid chloride gives almost a theoretical yield of 2,3-benzo-1-aza-9-oxo-fluorene [24]:



It is not as applicable to single ring compounds of nitrogen, although some arylated derivatives of lutidine carboxylic acid chloride and of pyridine dicarboxylic acid chloride have been cyclized by aluminum chloride.[25] 4-Phenyl-lutidine-3-carboxylic acid chloride gives a 70 per cent yield of 1,3-dimethyl-2-aza-fluorenone:



and 2,6-diphenyl-3,5-pyridine dicarboxylic acid chloride yields 2,3,5,6-dibenzoylenpyridine in similarly good yield:

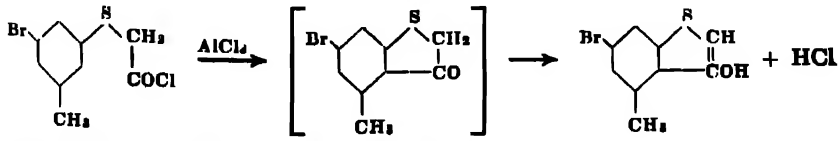


Intramolecular condensations of nitrogeneous carboxylic acid chlorides are listed in Table 19.

Intramolecular Ring Closure of Sulfur Compounds

Although ring closure of sulfur-containing aralkyl acid chlorides is a very useful step in the preparation of compounds of the thioindigo series, aluminum chloride has been little used for this purpose.

Aryl-substituted thioglycolic acid chlorides undergo intramolecular condensation to yield keto- or enol-thionaphthenes. Thus S-(5-bromo-3-methylphenyl)thioglycolic acid chloride gives a 35 per cent yield of 6-bromo-4-methyl-3-hydroxythianaphthene [26]:



[24] W. Borsche and F. Sinn, *Ann.*, **532**, 146-165 (1937).
[25] W. Borsche and H. Hahn, *Ann.*, **537**, 219-245 (1939).
[26] K. v. Auwers, *Ber.*, **53**, 2285-2299 (1920); *C. A.*, **15**, 1487.

(Text continued on p. 422)

Table 19.

ω-Halogeno-N-Acyl Amines

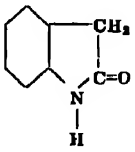
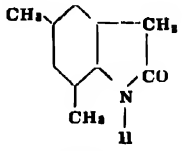
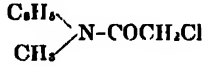
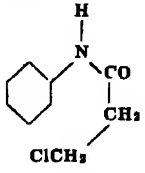
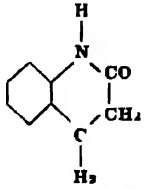
Acid Halide	Product	Yield	Ref
chloroacetanilide ($C_6H_5NHCOCH_2Cl$)	oxindole 	85%	1
chloroacet-*o*-toluidide (o-CH_3-$C_6H_4NHCOCH_2Cl$)	7-methyloxindole		1
chloroacet-*p*-toluidide	5-methyloxindole		1
chloroacet-*m*-xylidide $1,3$-$(CH_3)_2C_6H_3NHCOCH_2Cl$	5,7-dimethyloxindole 		5
chloroacet-*p*-xylidide	4,7-dimethyloxindole		5
N-methylchloracetanilide 	1-methyloxindole		1
N-ethylchloracetanilide	N-ethyloxindole		6
N-methyltrichloracetanilide	1-methyl-3,3-dichlorooxindole		1
N-phenyltrichloracetanilide	3,3-dichloro-1-phenyloxindole (this yields N-phenylisatin upon treatment with water)		1, 27
N-(β-chloropropionyl)-derivatives of arylamines, *e.g.*, anilide of β-chloropropionic acid chloride; 	Hydrocarbostyriles, *e g.*, 2-keto-tetrahydroquinoline 	95%	29
other arylides of β-chloropropionyl chloride include: *o*, *m*, and *p*-toluidine *o*- and *p*-chloroaniline 2,4-dichloroaniline *o*, *m*, and *p*-aminophenol *p*-phenitidine *p*-nitroaniline	condensation proceeds analogously (60–100% yields) with other mono-amines to yield correspondingly substituted 2-ketotetrahydroquinolines. With diamines, diketooctohydrophenanthrolines are formed in 80%		

Table 19—*(Continued)*

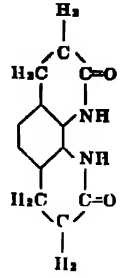
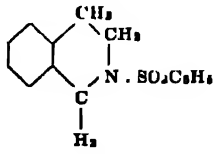
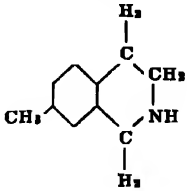
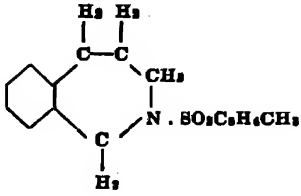
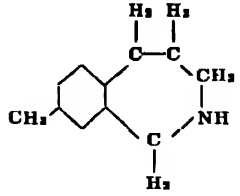
Acid Halide	Product	Yield	Ref.
o-, *m*-, and *p*-phenylenediamine diphenylamine	yield. From N,N'-*bis*-β-chloropropionyl-*o*-phenylenediamine is formed the following compound: 		
N-β-chlorobutyryl derivatives of arylamines: aniline *o*- and *p*-toluidine *o*- and *p*-chloroaniline 2,4-dichloroaniline *o*-phenylenediamine	Ketotetrahydroquinolines, *e.g.*, aniline yields 2-keto-4-methyltetrahydroquinoline; *o*-phenylenediamine yields 2,9-diketo-4,7-dimethyl-1,2,3,4,7,8,9,10-octohydrophenanthroline.	55–92%	20
	Arylated Glycyl Chlorides		
β-phenylethylmethylglycyl chloride $C_6H_5 . (CH_2)_2 . N(CH_3) . CH_2COCl$	N-methyltetrahydroisoquinoline	40%	11
$C_6H_5(CH_2)_2N(SO_2 . C_6H_5) . CH_2COCl$	benzenesulfonyl derivative of tetrahydroisoquinoline 	80%	12
$CH_3 . C_6H_4 . (CH_2)_2N . (SO_2 . C_6H_5) . CH_2COCl$	benzenesulfonyl derivative of methyltetrahydroisoquinoline: saponification yields 	65%	11,12
p-toluenesulfonyl derivative of N-phenylpropylglycyl chloride	*p*-toluenesulfonyl derivative of homotetrahydroisoquinoline	65%	12

Table 19—*(Continued)*

Acid Halide	Product	Yield	Ref.
$C_6H_5 . (CH_2)_2 . N(SO_2 . C_6H_4 . CH_3) . CH_2COCl$			
benzenesulfonyl derivative of $CH_3 . C_6H_4 . (CH_2)_2 . NH . CH_2COCl$	8-methyl-*as*-homotetrahydroisoquinoline (upon hydrolysis)	70%	11
			
benzenesulfonyl derivative of $(CH_3)_2CH . C_6H_4 . CH_2 . CH_2NH . CH_2COCl$	8-isopropyl-*as*-homotetrahydroisoquinoline (upon hydrolysis)	70%	11

Arylamine-Oxalyl Chloride Condensation Products

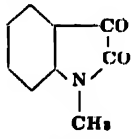
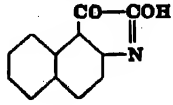
N-methyloxanilic acid chloride ($C_6H_5 . N(CH_3) . CO . COCl$)	1-methylpseudoisatin		1
			
N-ethyloxanilic acid chloride	1-ethylpseudoisatin		1, 23
N-di-*p*-tolyloxamic acid chloride	1-*p*-tolyl-5-methylpseudoisatin		1
benzyloxanilic acid chloride	1-benzylpseudoisatin		1
N-phenyloxanilic acid chloride	1-phenylpseudoisatin		28
N-(phenyl-α-naphthyl)oxamic acid chloride [$(C_{10}H_7)(C_6H_5)N . CO . COCl$]	1-phenyl-6,7-benzopseudoisatin		1
β-N-ethylaminonaphthalene + oxalyl chloride	N-ethyl-2,1-naphthisatin		24
β-naphthyloxamic acid chloride	2,1-naphthisatin	75–80%	14
			

Table 19—*(Continued)*

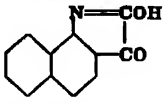
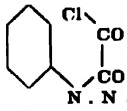
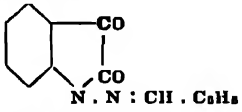
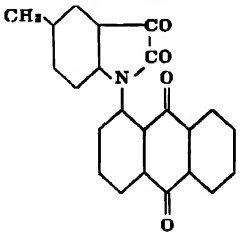
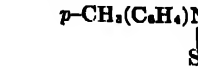
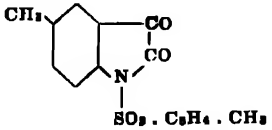
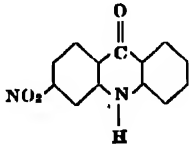
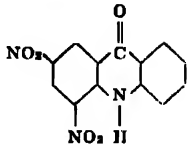
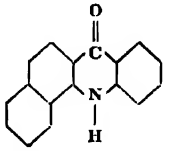
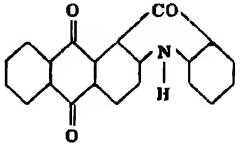
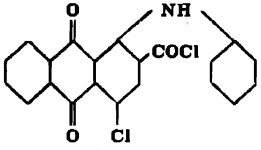
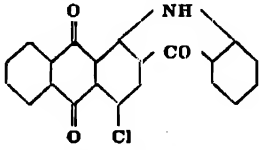
Acid Halide	Product	Yield	Ref.
α-naphthyloxamic acid chloride	1,2-naphthisatin 		14
benzalphenylhydrazine oxalyl chloride 	N-(benzylideneamino)-pseudoisatin 		8
N-monoarylamino-anthraquinones + oxalyl chloride; *e.g.*, 1-*p*-toluidino-anthraquinone + oxalyl chloride	N-anthraquinonylpseudoisatins *e.g.*, N-α-anthraquinonyl-5-methylpseudoisatin 		25
aceto-β-naphthylamide + oxalyl chloride	(?)-2-acetamideacenaphthenequinone		26
N-*p*-toluenesulfonyl derivative of N-*p*-tolyloxamic acid chloride 	N-*p*-toluenesulfonyl-5-methylpseudoisatin  (easily hydrolyzed to 5-methylisatin)		13
N-arylsulfonyl derivative of α-naphthylamine oxanilic acid chloride	1,8-naphthisatin (upon hydrolysis)		13
C-Acid Halides of Diarylamines			
5-nitrodiphenylamine-2-carboxylic acid chloride	2-nitroacridone 		7

Table 19—*(Continued)*

Acid Halide	Product	Yield	Ref.
5-chlorodiphenylamine-2-carboxylic acid chloride	2-chloroacridone		7
4,6-dinitrodiphenylamine-2-carboxylic acid chloride	1,3-dinitroacridone 		20
α-naphthylphenylamine-2-carboxylic acid chloride	1,2-benzacridone 		30
β-naphthylphenylamine-2-carboxylic acid chloride	2,3-benzacridone		30
anthraquinone-2-anilido-1-carboxylic acid chloride	anthraquinone-1,2-acridone 	93%	18,19,21
anthraquinone-1-anilido-4-chloro-2-carboxylic acid chloride 	4-chloroanthraquinone-2,1 acridone 	78%	17.21
arylaminoanthraquinone carboxylic acid chlorides	acridone derivatives		21

Acyl Halides of N-ring Compounds

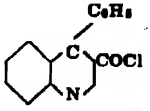
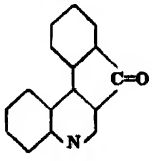
4-phenylquinoline-3-carboxylic acid chloride 	2,3-benzo-1-aza-9-ketofluorene (2 g from 2.5 g acid) 		10

Table 19—*(Continued)*

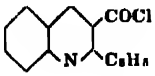
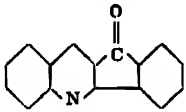
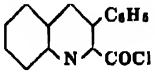
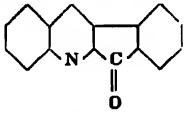
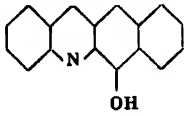
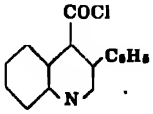
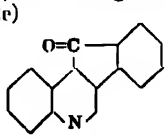
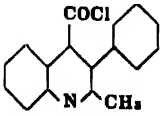
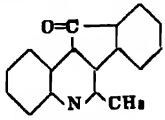
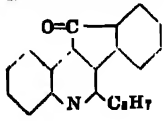
Acid Halide	Product	Yield	Ref.
2-phenylquinoline-3-carboxylic acid chloride 	2,3-benzo-4-aza-9-ketofluorene (almost theoretical yield) 		2
2-phenylquinoline-3-acetic acid chloride	yellow compound, m.p. 367-370° (contaminated with S from thionyl chloride)		2
3-phenylquinoline-2,4-dicarboxylic acid chloride	2,3-benzo-1-aza-9-ketofluorene-4-carboxylic acid and 1,2-benzo-3-aza-9-ketofluorene-4-carboxylic acid		4
3-phenylquinaldinic acid chloride 	2,3-benzo-1-aza-9-ketofluorene (1.2 g from 2.49 g acid) 		4
3-benzylquinaldinic acid chloride	2,3-benzo-1-azanthran-9-ol 	90%	4
3-phenylcinchonic acid chloride 	1,2-benzo-3-aza-9-ketofluorene (1.8 g from 2.68 g acid chloride) 		4
2-methyl-3-phenylcinchonic acid chloride 	4-methyl-9-keto-1,2-benzo-3-azafluorene (0.65 g from 2.5 g acid) 		22
2-isopropyl-3-phenylcinchonic acid chloride	4-isopropyl-1,2-benzo-3-azafluorenone (1.84 g from 2 g acid) 		2

Table 19—*(Continued)*

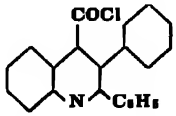
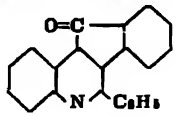
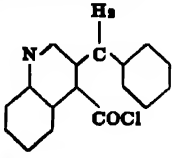
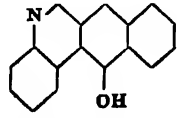
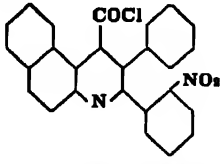
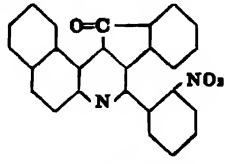
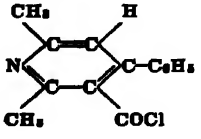
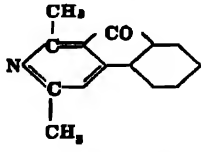
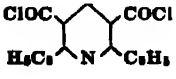
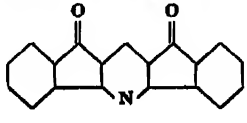
Acid Halide	Product	Yield	Ref.
3-phenyl-2-chlorocinchonic acid chloride	4-chloro-1,2-benzo-3-azafluorenone (almost theoretical yield of the crude ketone)		2
2,3-diphenylcinchonic acid chloride 	4-phenyl-9-keto-1,2-benzo-3-azafluorene (5.8 g from 6.5 g acid) 		22
3-phenyl-5,6-benzocinchonic acid chloride	1,2(1,2)-naphtho-3-aza-9-keto-fluorene (2.7 g from 3 g acid)		2
2,3-diphenyl-5,6-benzocinchonic acid chloride	4-phenyl-1,2(1,2)-naphtho-3-aza-9-ketofluorene		2
3-benzylcinchonic acid 	1,2-benzo-3-azaanthran-9-ol 	80%	4
2-(2′-nitrophenyl)-3-phenyl-5,6-benzocinchonic acid chloride 	4-(2′-nitrophenyl)-1,2(1′,2′)-naphtho-3-azafluorenone (3.6 g from 4.2 g acid) 		9
4-phenyllutidine-3-carboxylic acid chloride 	1,3-dimethyl-2-azafluorenone 	70%	3
4-(p-methoxyphenyl)lutidine-3-carboxylic acid chloride	1,3-dimethyl-7-methoxy-2-azafluorenone (2.3 g from 2.6 g acid)		3
2,6-diphenylpyridine-3,5-dicarboxylic acid chloride 	2,3,5,6-dibenzoylenepyridine (2.3 g from 3.2 g acid) 		3

Table 19—*(Concluded)*

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2. W. Borsche and F. Sinn, *Ann.*, 532, 166-185 (1937).
3. W. Borsche and H. Hahn, *Ann.*, 537, 216-245 (1939).
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10. W. Borsche and F. Sinn, *Ann.*, 538, 283-292 (1939).
11. J. v. Braun and K. Wirz, *Ber.*, 60, 102-110 (1927).
12. J. v. Braun, G. Blessing, and R. S. Cahn, *Ber.*, 57, 908 (1924).
13. Brit. P. 265,824 (1927) to I. G.; *Brit. Chem. Abs.*-B, 224 (1928).
14. Brit. P. 286,358 (1928) to I. G., *Brit. Chem. Abs.*-B, 327 (1928); German P. 448,946, *C. Z.*, 1927, II, 2228; Brit. P. 303,740 to I. G.
15. J. v. Braun, K. Heider, and E. Muller, *Ber.*, 50, 1637-1651 (1917); *J. Chem. Soc. Abs.*, 114, 107 (1918).
16. A. Kliegl and A. Fehrle, *Ber.*, 47, 1629-1640 (1914).
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18. F. Ullmann and M. Sone, *Ann.*, 380, 336-341 (1911).
19. F. Ullmann, *Ber.*, 43, 536-539 (1910).
20. F. Ullmann, W. Bader, and H. Labhardt, *Ber.*, 40, 4795-4799 (1907).
21. German P. 237,236 (1911) to Badische Alinin und Soda-Fabrik.; *C. Z*, 1911, II, 735.
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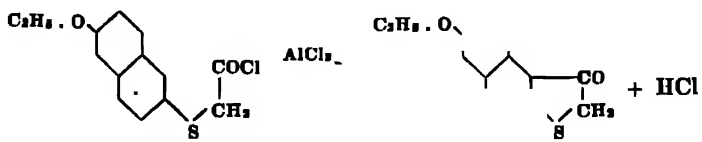
23. R. Stollé, *Ber.*, 46, 3915-3916 (1913); *C. A.*, 8, 708. German P. 281,046 (1913) to R. Stollé; *C. A.*, 9, 1999.
24. Swiss P. 92,688, 93,486, 93,489 to H. Staudinger; *C. Z.*, 1923, II, 573.
25. German P. 282,490 (1915) to Farbenfabrik vorm. F. Bayer & Co.; *J. Chem. Soc. Abs.*, 108 (I), 839 (1915); *C. Z.*, 1915, I, 553.
26. G. Gallas and G. Bermudez, *Anal. Fis. Quim.*, 29, 464-469 (1931); *Brit. Chem. Abs.*-A, 1284 (1931).
27. German P. 341,112 to R. Stollé.
28. German P. 281,045 to R. Stollé.
29. F. Mayer, L. van Zütphen, and H. Phillips, *Ber.*, 60, 858-864 (1927).
30. F. Ullmann, *Ann.*, 355, 312-358 (1907).

A 75 per cent yield of 3-hydroxythianaphthene-7-carboxylic acid chloride is secured from S-(*o*-carboxyphenyl)thioglycolyl chloride by treatment with aluminum chloride. Ring closure also occurs more readily as the molecular weight of the aryl residue is increased, the *keto*- derivative of the thianaphthene being obtained. Thus, 6-ethoxynaphthalene-2-thioglycolic acid chloride gives an 80 per cent yield of the corresponding *keto*-dihydrothianaphthene [27]:



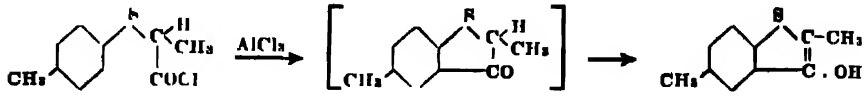
Treatment of S-benzylthioglycolic acid chloride results in the formation of the expected six-membered ring.[28]

The crude product resulting from the action of aluminum chloride on arylthioglycolic acid chlorides may be directly condensed with halogenated isatins to give indigoid dyes.[29]

Ring closure of α-alkyl-S-arylthioglycolic acid chlorides with aluminum chloride does not proceed readily. Thus α-*p*-thiocresylisopropionyl

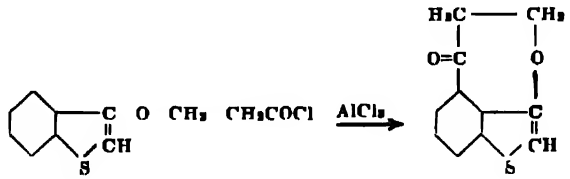
[27] U. S. P. 1,765,703 (1930) to E. Runne, K. Moldaenke, and E. Fischer (to General Aniline Works), *C. A.*, 24, 4057; German P. 515,541 (1927) to E. Runne, K. Moldaenke, and E. Fischer (to I. G.), *C. A.*, 25, 2443; British P. 298,498 (1927) to I. G. Farbenindustrie, *C. A.*, 23, 3109.
[28] R. Lesser and A. Mehrlander, *Ber.*, 56, 1643-1648 (1923); *J. Chem. Soc. Abs.*, 124 (I), 827 (1923).
[29] U. S. P. 2,003,161 to W. Hayes (to du Pont); *C. A.*, 31, 4581.

chloride yields only a very small amount of a product which is probably 2,5-dimethyl-3-hydroxythianaphthene [26]:



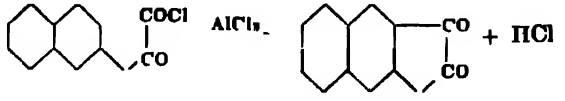
β-Arylmercaptopropionyl chlorides undergo ring closure to thiochromanones even in the cold with concentrated sulfuric acid;[30] but little is known concerning the use of aluminum chloride for this type of condensation. Lack of interest may be due to the fact that, whereas chromanones may be obtained by the condensation of phenol ethers with β-bromopropionyl chlorides in the presence of aluminum chloride,[31] like reaction with arylmercaptans does not afford a promising method for the production of thiochromanones.

β-(3-thianaphthenoyl)propionyl chloride undergoes ring closure, as do β-aroylpropionyl chlorides [32]:



Aluminum chloride has been reported to be inferior to phosphorus pentoxide or phosphoryl chloride for effecting ring closure to thioflavones,[33] although it does catalyze the formation of thioflavone from β-phenylthiocinnamoyl chloride [34]

The condensation product of thiocresol with oxalyl chloride yields methylthianaphthenequinone upon treatment with aluminum chloride,[35] and similarly β-thianaphthisatin is obtained from β-thianaphthyloxalyl chloride [36]:



Thioquinones may be prepared in good yield by treating *keto*- acids of thianaphthene with a halogenating agent and subsequent ring closure with aluminum chloride. Benzothiophanthrenequinone is thus obtained

(Text continued on p 427)

[30] F. Krollpfeiffer and H. Schultze, *Ber.*, 56, 1819-1824 (1923).
[31] K. v. Auwers and E. Lämmerhirt, *Ann.*, 421, 1-58 (1920); *C. A.*, 14, 2629.
[32] F. Krollpfeiffer and K. Schneider *Ber.*, 61, 1284-1291 (1928)
[33] F. Arndt, *Ber.*, 56, 1269-1279 (1923).
[34] S. Ruhemann, *Ber.*, 46, 2188-2197 (1913)
[35] R. Stolle, *Ber.*, 47, 1120-1123 (1914).
[36] British P. 186,869 (1921) to Soc. anon. pour l'ind. chim. a Bâle, *C. A.*, 17, 1029, British P 214,894 (1923) to Soc. anon. pour l'ind. chim. a Bâle, *C. A.*, 18, 2513

Table 20.

Acid Halids

S-Aryl Thioglycolic Acid Halides

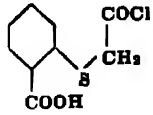
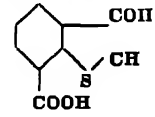
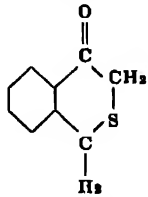
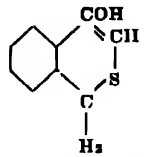
	Product	Yield	Ref.
(6-carboxyphenyl)thioglycolyl chloride 	3-hydroxythianaphthene-7-carboxylic acid 	75%	7
(3-chloro-6-carboxyphenyl)-thioglycolyl chloride	4-chloro-3-hydroxythianaphthene-7-carboxylic acid		7
(5-bromo-3-methylphenyl)-thioglycolyl chloride 5,3-$BrCH_3C_6H_3SCH_2COCl$	6-bromo-4-methyl-3-hydroxythianaphthene	35%	12
β-naphthylthioglycolyl chloride	3-thiophanthrenone		15
1-methyl-2-naphthylthioglycolyl chloride	9-methyl-3,(2)-thiophanthrenone		10
1-halo-2-naphthylthioglycolyl chloride	9-halo-3,(2)-thiophanthrenone		11
arylthioglycolyl halides, *e.g.*, 8-chloro-1-naphthylthioglycolyl chloride ($RSCH_2COX$, where R is any residue)	hydroxythianaphthenes, *e.g.*, 8-chloro-1,2-naphthothioindoxyl		3
alkoxyarylthioglycolyl chloride, *e.g.*, 6-ethoxynaphthyl-2-thioglycolyl chloride	alkoxy-3-ketodihydrothianaphthenes, *e.g.*, 6-ethoxy-4,5-benzo-3-keto-dihydrothianaphthene	80%	4,6
benzylthioglycolyl chloride $C_6H_5 . CH_2 . S . CH_2COCl$	4-ketoisothiochroman (2 g from 5 g acid)  or, 4-hydroxyhomothianaphthene 		2
α-*p*-thiocresylpropionyl chloride $4-CH_3 . C_6H_4 . S . CH(CH_3) . COCl$	2,5-dimethyl-3-hydroxythianaphthene (?)	very small	12

Table 20—*(Continued)*

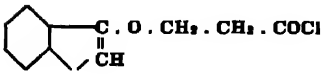
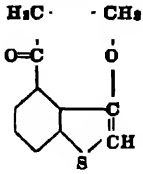
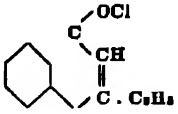
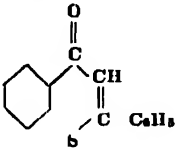
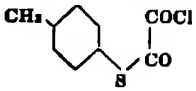
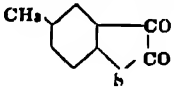
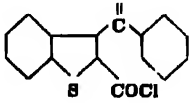
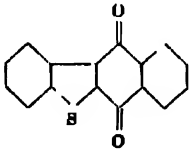
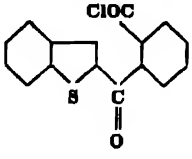
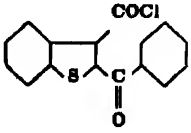
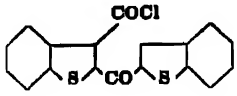
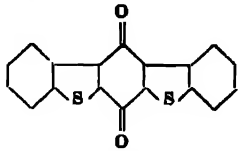
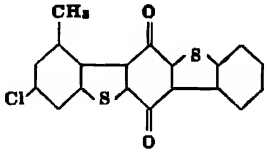
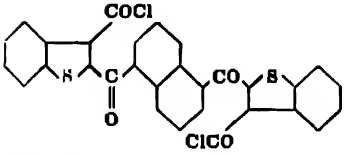
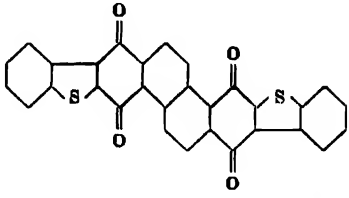
Acid Halide	Product	Yield	Ref
β-(3-thianaphthenoyl)-propionyl chloride 	2,3-thianaphthene-4-keto-5, 6-dihydropyran 		1
β-phenylthiocinnamoyl chloride 	thioflavone 		5
thiocresyl oxalyl chloride 	methylthianaphthenequinone 		8
β-thianaphthyl oxalyl chloride	β-thianaphthisatin		13,14
3-benzoylthianaphthene-2-carboxylic acid chloride 	benzothiophanthrenequinone 	90%	9
2-(thianaphthenoyl)benzoyl chloride 	benzothiophanthrenequinone		9
2-benzoylthianaphthene-3-carboxylic acid chloride 	benzothiophanthrenequinone	76%	9

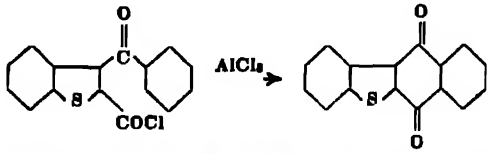
Table 20—*(Concluded)*

Acid Halide	Product	Yield	Ref.
2,2′-dithianaphthenyl ketone-3-carboxylic acid chloride 	dithianaphthenylenequinone 	88%	9
4-methyl-6-chloro-2,3′-dithianaphthenyl-ketone-2′-carboxylic acid chloride	*p*-(S)-2-methyl-4-chloro-dithianaphthenylquinone 	78%	9
naphthalene-1,5-(2,2′, dithianaphthenoyl-3,3′-dicarboxylic acid chloride 	1,2-*bis*-benzothiophanthrene-quinone 	86%	9

References

1. F. Krollpfeiffer and K. Schneider, *Ber.*, 61, 1284-1291 (1928); *Brit. Chem. Abs.-A*, 896 (1928).
2. R. Lesser and A. Mehrlander, *Ber.*, 56, 1642-1648 (1923); *J. Chem. Soc. Abs.*, 124 (I), 837 (1922).
3. Swiss P. 168,447 (1934) to Soc. pour l'ind. chim. a Bâle; *C. A.*, 29, 614.
4. U. S. P. 1,765,703 (1930) to E. Runne, K. Moldaenke, and E. Fischer (to General Aniline Works), *C. A.*, 24, 4057 (1930); German P. 515,541 (1927) to E. Runne, K. Moldaenke, and E. Fischer (to I. G.), *C. A.*, 25, 2442.
5. S. Ruhemann, *Ber.*, 46, 2185-2197 (1913).
6. British P. 268,493 (1927) to I. G. Farbenindustrie; *C. A.*, 23, 3109.
7. German P. 530,331 (1931) and British P. 360,349 (1931) to I. G. Farbenindustrie; *C. Z.*, 1932, I, 740.
8. R. Stollé, *Ber.*, 47, 1130-1132 (1911).
9. F. Mayer, A. Mombour, W. Lassmann, W. Werner, P. Landmann, and E. Schneider, *Ann.*, [illegible]
10. Swiss P. 134,093 (1927) to Soc. anon. pour l'ind. chim. a Bâle; *C. A.*, 24, 1745.
11. German P. 495,448 (1927) to Soc. anon. pour l'ind. chim. a Bâle; *C. A.*, 24, 3251.
12. K. v. Auwers, *Ber.*, 53, 2285-2299 (1920); *C. A.*, 15, 1457.
13. British P. 186,859 (1921) to Soc. anon. pour l'ind. chim. a Bâle; *C. A.*, 17, 1029.
14. British P. 214,864 (1923) to Soc. anon. pour l'ind. chim. a Bâle; *C. A.*, 18, 2813.
15. U. S. P. 2,063,161 (1936) to E. Havas (to du Pont); *C. A.*, 31, 881.

in 90 per cent yield from 3-benzoylthionaphthene-2-carboxylic acid chloride [87]:



[87] F. Mayer, A. Mombour, W. Lassmann, W. Werner, P. Landmann, and E. Schneider, *Ann.*, 488, 250-296 (1931).

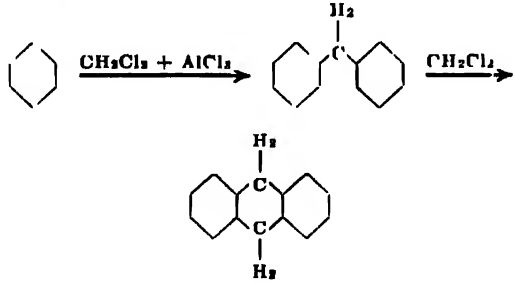
Intramolecular ring closures of thio- compounds effected by treatment with aluminum chloride are summarized in Table 20.

Intermolecular Ring Closure

Instances of intermolecular ring closure, with evolution of hydrogen chloride, are pointed out throughout the discussion of Friedel-Crafts reactions found in this book, and individual cases will not be described here. Ring closures of this type may be generalized as occurring in

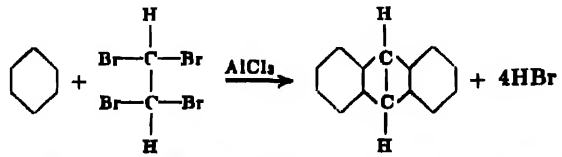
(1) hydrocarbon synthesis
(2) ketone synthesis

The formation of polynuclear compounds is frequently mentioned, especially by earlier workers, in connection with the Friedel-Crafts condensation of aromatic hydrocarbons and polyhalogenated alkyl or aralkyl halides. Anthracene dihydride, or its derivatives, is formed together with normal alkylation products in the condensation of benzene or its homologs with methylene chloride, ethylidene bromide, ethylidene chloride, vinyl bromide, chloroform, benzal chloride, and benzyl chloride The formation of anthracenes from methylene chloride has been explained as proceeding through intermediate formation of diarylmethanes [38]:



The intermediate formation of anthracenedihydrides, and their dehydrogenation to anthracene under the action of aluminum chloride, has been assumed.[39] Since the other halides mentioned above also yield diarylmethanes upon condensation with aromatic hydrocarbons, the formation of anthracenes with these halides may also be explained in the same way However, other theories have been advanced.

The production of anthracene from benzene and *sym*-tetrabromoethane may occur according to the scheme [40]:



[38] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 11, 263-277; *J. Chem. Soc. Abs.*, 52, 1102 (1887). J. Lavaux, *Compt. rend.*, 140, 44-45 (1905); *J. Chem. Soc. Abs.*, 128 (1905) (1)
[39] R. Anschütz, *Ann.*, 235, 299-341 (1886).
[40] R. Anschütz and F. Eltsbacher, *Ber.*, 16, 1435-1446 (1883).

Methylated anthracenes are formed when toluene or the xylenes are used instead of benzene in the foregoing reaction; but with ethylbenzene no ethylanthracene is obtained.[41]

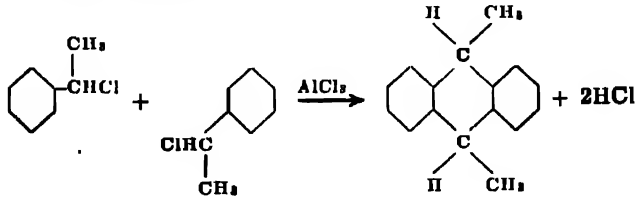
Other products of the reaction with benzene and *sym*-tetrabromoethane were bromobenzene, *asym*-diphenylethane, and anthraquinone.[42] The formation of bromobenzene indicates cleavage of bromine from the tetrabromide. The diphenylethane may have been formed by reaction of benzene with the partially debrominated compound. It has been shown that by the action of aluminum chloride on *sym*-tetrabromoethane there is formed 1,1-dibromo-2-bromoethane. However, direct condensation of this compound with benzene and aluminum chloride yields dibenzyl.[43]

Another possible explanation for the formation of *asym*-diphenylethane and anthracene in the reaction is the primary formation of a halogenated aralkyl hydrocarbon by reaction of the aromatic hydrocarbon with acetylene tetrabromide. The following could have been thus formed:

β-bromostyrene dibromide, $C_6H_5CHBr.CHBr_2$
stilbene bromide, $C_6H_5CHBr.CHBr.C_6H_5$
tolane dibromide, $C_6H_5.CBr:CBr.C_6H_5$

Condensation of these products with benzene and aluminum chloride, however, was found to yield only symmetrical tetraphenylethane; therefore, they could not have been intermediates in the formation of anthracene.

The production of anthracene derivatives may be due to intermediate formation of a halogenated alkyl derivative of benzene. Aluminum chloride has been shown to react on α-chloroethylbenzene to yield *meso*-dimethyldihydroanthracene[44]:

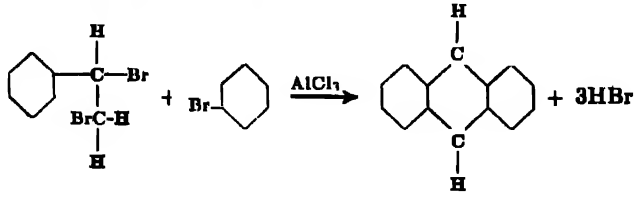


asym-Diphenylethane is a by-product of the reaction. Both of these compounds are formed in the reaction of ethylidene chloride with benzene and aluminum chloride.[45] This condensation can then be explained by assuming preliminary decomposition of ethylidene chloride to vinyl chloride, reaction of the latter with benzene to yield α-chloroethylbenzene, and subsequent condensation as above.

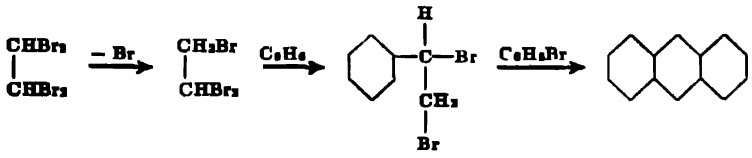
Anthracene has been shown to be the product of the condensation of α,β-dibromoethylbenzene and benzene with aluminum chloride. Since

[41] R. Anschütz and H. Immendorff, *Ber.*, 17, 2816-2817 (1884).
[42] R. Anschütz, *Ann.*, 235, 150-220 (1886).
[43] R. Anschütz, *Ann.*, 235, 333 (1886).
[44] J. Schramm, *Ber.*, 26, 1706-1709 (1893).
[45] R. Anschütz and E. Romig, *Ber.*, 18, 662-666 (1885). R. Anschütz, *Ann.*, 235, 302-307 (1886).

bromobenzene is also one of the reaction products, this condensation may proceed according to the scheme:



Bibenzyl is also formed in the reaction. However, if styrene, the dehalogenated product, is heated with benzene and aluminum chloride on a water-bath, *asym*-diphenylethane is formed. The course of the above condensation somewhat parallels that of acetylene tetrabromide and benzene so that the following sequence for the two reactions may be assumed:



$$C_6H_5.CHBrCH_2Br \xrightarrow{-2Br} C_6H_5.CH:CH_2 \xrightarrow{C_6H_6 + AlCl_3} (C_6H_5)_2CH\ CH_3$$

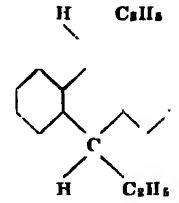
Other instances in the literature cite self-condensation of halogenated hydrocarbons in the presence of aluminum chloride. Benzyl chloride condenses with itself to give a low yield of anthracene.[46] A 4 per cent yield of perylene has been secured by the action of aluminum chloride on 1-bromonaphthalene.[47] 9-Bromophenanthrene yields some 2,3,10-11-dibenzoperylene.[48] Since long heating with the catalyst is generally necessary to bring about reaction, the mechanism of such condensations may resemble that of the Scholl synthesis in which aluminum chloride has a dehydrogenating action. Such dehydrogenating action is seen in the anthracene syntheses cited above, for the intermediate anthracene dihydrides are converted to anthracenes during the reaction, although the fate of the hydrogen evolved is not indicated.

An instance of such dehydrogenating activity has been more recently confirmed in a study of the reaction of allyl chloride with benzene and aluminum chloride.[49] The condensation with an anhydrous catalyst yields 1,2-diphenylpropane, addition of phenyl taking place at the double bond as well as by replacement of halogen, an intermediate product being chloropropyl benzene:

$$C_6H_6 + ClCH_2.CH:CH_2 \xrightarrow{-HCl} C_6H_5.CH_2.CH:CH_2$$
$$\xrightarrow{+HCl} C_6H_5.CH_2.CHCl.CH_3$$

[46] J. Lavaux and M. Lombard, *Bull. soc. chim. (4)*, 7, 539-542 (1910); *C. A.*, 4, 2448.
[47] R. Weitzenbock and C. Barr, *Ber.*, 46, 1994-2000; *C. A.*, 7, 2947.
[48] E. Clar, *Ber.*, 68, 542-550 (1932); *C. A.*, 26, 4046.
[49] C. D. Nenitzescu and D. A. Isacescu, *Ber.*, 66, 1100-1106 (1933).

If a hydrated, or weakened catalyst is used, the (chloropropyl)benzene undergoes self condensation to give diethyldihydroanthracene,

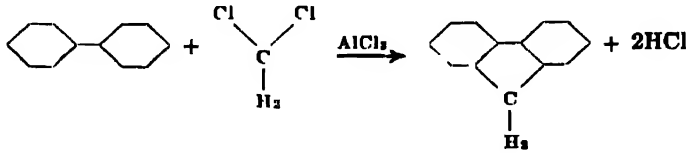


which is dehydrogenated, as are other dihydroanthracenes reported in the literature, to give diethylanthracene, in this case. The hydrogen evolved serves to dehalogenate some of the (chloropropyl)benzene,

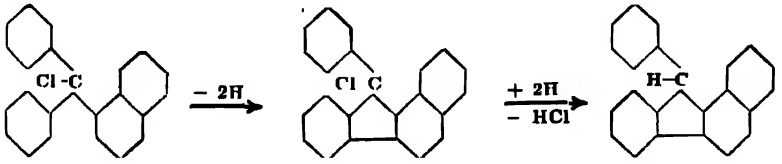
$$C_6H_5 . CH_2 . CHCl . CH_3 \xrightarrow{+\,2H} C_6H_5CH_2CH_2CH_3 + HCl$$

With a weakened catalyst the reaction products of allyl chloride and benzene are therefore *n*-propylbenzene and diethylanthracene.

Such hydrogenating-dehalogenating activity has probably occurred in the synthesis of fluorene derivatives which has been recently cited. Diphenyl with dichloromethane and aluminum chloride has been reported to yield fluorene: (See page 110).



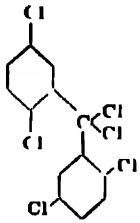
However, a *peri*-ring closure does not occur in the condensation of naphthalene or α-naphthol with diphenyldichloromethane. Instead, the primarily formed naphthyldiphenylchloromethane undergoes a dehydrogenation with simultaneous formation of a five-membered ring [50]:



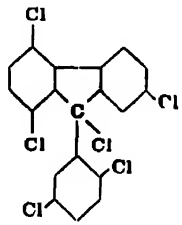
An almost theoretical yield of 3-hydroxy-9-phenyl-1,2-benzofluorene is thus obtained by condensation of α-naphthol with diphenyldichloromethane.

[50] E. Clar, *Ber.*, **63**, 813-817 (1930); *C. A.*, **24**, 3007.

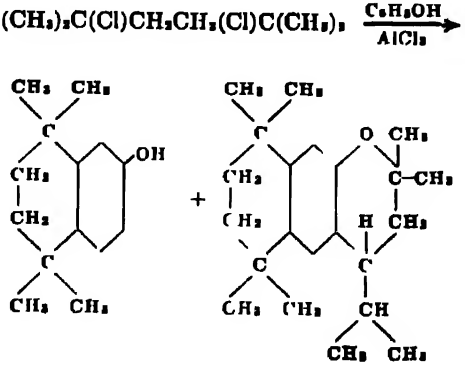
An unusual course is taken in the condensation of carbon tetrachloride with *p*-dichlorobenzene at 55° for ten hours.[51] At room temperature the product is 2,5,2′,5′-tetrachlorobenzophenone chloride,



but at 55°, another molecule of *p*-dichlorobenzene is added, with formation of a phenyl fluorene derivative probably having the structure·



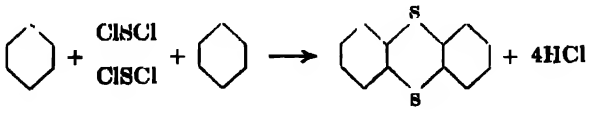
Di-tertiary 1,4-dichlorides, *e g*, 2,5-dichloro-2,5-dimethylhexane, condense in the presence of aluminum chloride with aromatic hydrocarbons, phenols, or phenol ethers so as to introduce a new hydroaromatic cycle into the aromatic nucleus. Phenol thus gives an 80 per cent yield of 5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-2-naphthol, together with a chromane derivative, produced by further reaction of the first product[52]



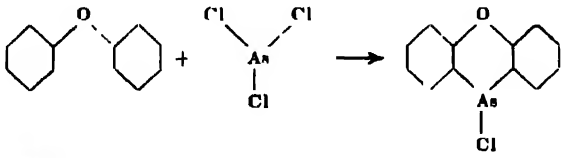
Arsenic and sulfur halides react as do dichloromethanes in that two

[51] S. D. Wilson and Hsiao-Yun Huang, *J. Chinese Chem. Soc.*, 4, 143-148 (1936); *C. Z.*, 1936, II 3788; c. f. S. D. Wilson and Y. Y. Cheng, *J. Org. Chem.*, 5, 223-8 (1940).
[52] H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, 62, 38-44 (1940).

halogens may be displaced for formation of cyclic products; benzene and sulfur dichloride yield thianthrene [53]:



and diphenyl ether with arsenic trichloride yields 5-chlorophenoxarsine:

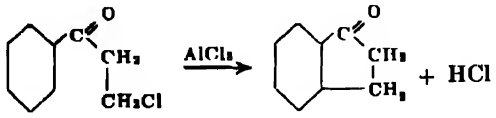


Ketone Synthesis

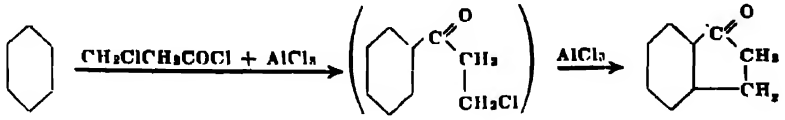
Acid halides which react with aromatic compounds and aluminum chloride to yield ring ketones may be classified as

(1) Halogenated aliphatic or aralkyl acid halides
(2) Unsaturated aliphatic or aralkyl acid halides
(3) Aliphatic dicarboxylic acid halides
    (a) Malonyl halides
    (b) Oxalyl halides
    (c) Diarylimido chlorides
(4) Aromatic carboxylic acid halides

Halogenated Acid Chlorides.—Intramolecular ring closure of ω-halogenoacyl hydrocarbons has already been discussed,†

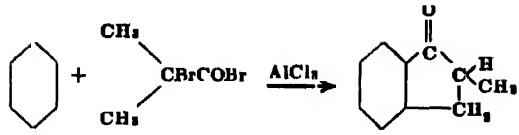


and it is to be expected that under certain conditions ring closure may occur during ketone synthesis without intermediate isolation of the open chain ketone:

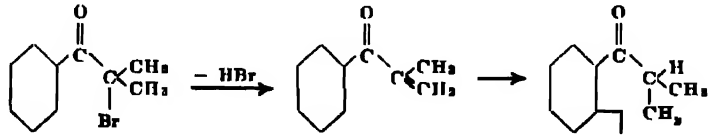


An interesting reaction is that of α-bromoisobutyryl bromide with benzene with production of 2-methyl-1-hydrindone [55]:

[53] E. Krafft and R. E. Lyons, *Ber.*, 29, 435-443 (1896); *J. Chem. Soc. Abs.*, 70, 297 (1896). K. Fries and W. Vogt, *Ann.*, 381, 313-337 (1911).
[54] W. Lewis, C. D. Lowry, and F. H. Bergeim, *J. Am. Chem. Soc.*, 43, 891-896 (1921).
† See page 394.
[55] N. Kishner, *J. Russ. Phys.-Chem. Soc.*, 46, 1411-1427 (1914); *C. Z.*, 1915, I, 1114.

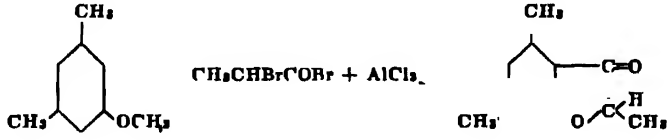


Since isopropenyl phenyl ketone was a by-product, the reaction may have proceeded as follows:

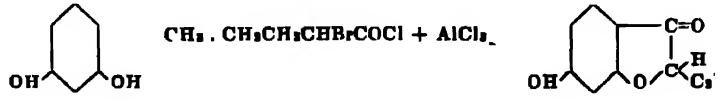


The condensation of trichloroacetyl chloride with benzene has been reported to yield fluorene-2-carboxylic acid.[56] The mechanism of the reaction has not been investigated.

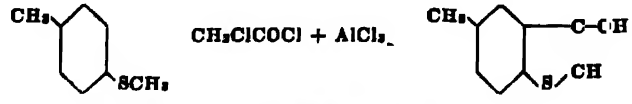
In the condensation of phenol ethers with halogenated acid chlorides for the production of coumaranones, ring closure is favored by the presence of substituents in the *meta*- position to the oxygen, and hindered by *ortho*- and *para*- substituents.[57] Thus *sym*-*m*-xylenol methyl ether and α-bromopropionyl bromide gives a 60-70 per cent yield of 1,3,5-trimethylcoumaranone[58]:



With resorcinol and α-bromovaleryl chloride, 1-propyl-5-hydroxycoumaranone is formed:



Condensation of chloroacetyl chloride with *p*-thiocresol methyl ether results in the formation of 5-methyl-3-hydroxythianaphthene in good yield[59]:



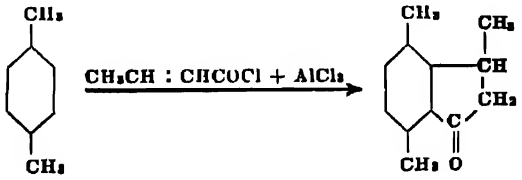
[56] M. Delacre, *Bull. soc. chim. (3)*, 27, 575 (1902).
[57] K. v. Auwers, *Ber.*, 49, 809-819 (1916); *Ann.*, 421, 59, 108 (1920).
[58] K. v. Auwers and W. Muller, *Ber.*, 50, 1149-1177 (1917).
[59] K. v. Auwers and F. Arndt, *Ber.*, 42, 537-545 (1909).

The analogous reaction with 2-naphthyl methyl sulfide instead of *p*-thiocresol methyl ether proceeds very slowly, only a small yield of 3-hydroxy-4,5-benzothianaphthene being secured.[60]

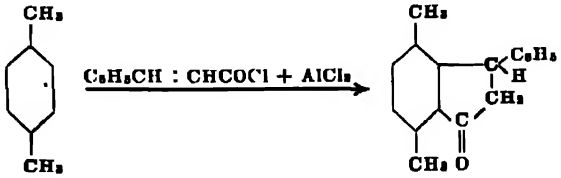
The preparation of thiochromanones by the reaction of *β*-bromopropionyl chloride with 2-naphthyl methyl sulfide in the presence of aluminum chloride has also been attempted, but the method shows little promise. Only traces of 5,6-benzothiochromanone were obtained.[60]

Ring closure during Friedel-Crafts acylation with halogenated acyl halides, or with unsaturated acid halides, required the presence in the ring of favorably located activating groups. If the entering acyl group goes *meta-* to an alkyl, alkoxy-, or hydroxy- group already present in the ring, closure may occur without isolation of the intermediate open-chain ketone. The presence of several activating groups facilitates reaction.

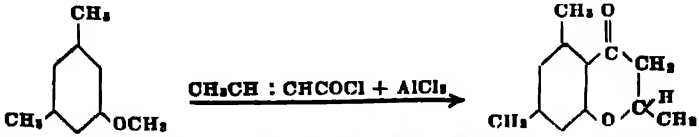
Unsaturated Aliphatic Acid Halides.—Acid halides of unsaturated carboxylic acids may react with substituted benzenes and aluminum chloride to give heterocyclic compounds. Thus *p*-xylene and crotonyl chloride give 3,4,7-trimethyl-1-hydrindone, together with the straight-chain acyl derivative.



Ring closure takes place at the double bond. With cinnamoyl chloride, phenylhydrindones are obtained [61]:



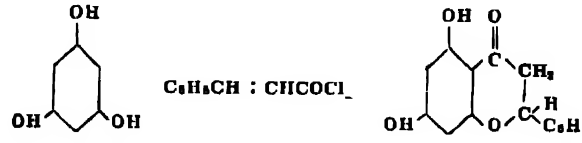
Substituted phenol ethers with crotonyl chloride yield chromanones. *sym-m*-Xylenol methyl ether thus gives 2,5,7-trimethylchromanone [62]:



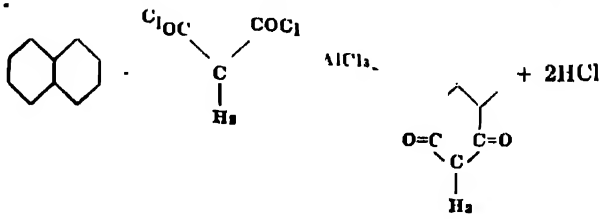
[60] F. Krollpfeiffer and H. Schultz, *Ber.*, 56, 1819-1824 (1923); F. Krollpfeiffer, H. Schultze, E. Schlumbohm, and E. Sommermyer, *Ber.*, 58, 1554-1576 (1925).
[61] K. v. Auwers and E. Risse, *Ann.*, 502, 282-290 (1933); *C. A.*, 27, 3470 (1933).
[62] K. v. Auwers and R. Döll, *Ann.*, 421, 86-103 (1920); *C. A.*, 14, 3694.

β,β-Dimethylacrylyl chloride undergoes like condensation, yielding 2,2,5,7-tetramethylchromanone.

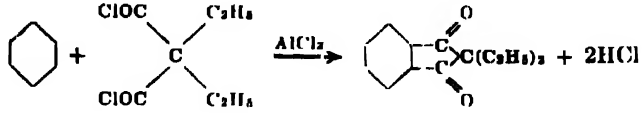
Cinnamoyl chloride or its derivatives yields flavanones with phloroglucinol[63]:



Malonyl Halides.—The condensation of malonyl halides or their alkyl derivatives with aromatic hydrocarbons and aluminum chloride for the production of indandiones has been extensively studied. The condensation occurs more readily with alkyl malonyl halides than it does with the unsubstituted malonyl halides; moreover, it was found that diethylmalonyl chloride is more reactive than is the dimethyl derivative. Malonyl chloride or bromide condenses only with polynuclear hydrocarbons and such highly activated benzene derivatives as di- or polysubstituted phenols or phenol ethers. With naphthalene, 1,3-*peri*-naphthindandione is formed[64]:



Diethylmalonyl chloride has been shown to yield indandiones with benzene, numerous alkyl benzenes, and phenol ethers. Excellent yields have been obtained in the condensation with benzene:



The reaction gives 72 g of 2,2-diethylindan-1,3-dione from 59.1 g of the acid chloride and 24 g of benzene. With benzene derivatives and with polynuclear hydrocarbons the condensation is complicated by the formation of two or more isomeric indandiones.

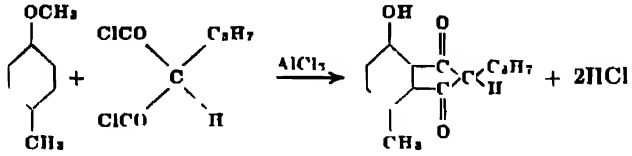
Recently, the condensation of mono-alkyl malonyl chlorides with phenol ethers has been studied.[65] Condensation with resorcinol ethers

[63] J. Shinoda and S. Sato, *J. pharm. Soc. Japan*, 48, No. 558, 109-114; No. 560, 117-120 (1928). *Brit. Chem. Abs.*-A, 199 (1929); *ibid.*, 48, 791-801 (1928), *C. A.*, 23, 536; *ibid.*, 51, 71-82 (1931), *Brit. Chem. Abs.*-A, 1162 (1931). J. Shinoda, M. Kawagoye, and D. Sato, *ibid.*, 51, 23-25 (1931); *Brit. Chem. Abs.*-A, 1162 (1931).

[64] K. Fleischer and E. Retze, *Ber.*, 55, 3280-3290 (1922); *J. Chem. Soc. Abs.*, 122 (I), 1138 (1923).

[65] T. K. Walker, A. J. Suthers, L. L. Roe, and H. Shaw, *J. Chem. Soc.*, 514-520 (1931); *Brit. Chem. Abs.*-A, 622 (1931). R. Black, H. Shaw, and T. K. Walker, *J. Chem. Soc.*, 272-279 (1931), *Brit. Chem. Abs.*-A, 487 (1931).

and with naphthol ethers gives unerystallizable resinous products. With *p*-cresol and with *p*-tolyl methyl ether well-defined hydroxyindandiones were obtained in good yields. Thus *p*-tolyl methyl ether with *n*-propylmalonyl chloride gives a theoretical yield of 4-hydroxy-7-methyl-2-*n*-propylindan-1,3-dione:



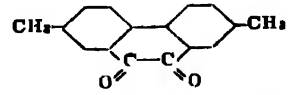
The use of the corresponding phenols results in slightly lower yields. The type of alkyl substituent in the malonyl chloride was found to have an influence on the yield. Best results were obtained with propylmalonyl and butylmalonyl chlorides. Malonyl chloride itself gives a 50 per cent yield of the corresponding hydroxyindandione from *p*-tolyl methyl ether. Branching of the alkyl chain resulted in low yields. Isopropylmalonyl chloride gave only a 16 per cent yield of the indandione from *p*-cresol.

Condensations effected with malonyl halides have been summarized in Table 21.

Oxalyl Chloride.—Oxalyl chloride condenses with aromatic compounds to yield four types of products:

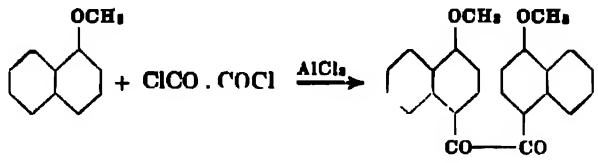
(1) Carboxylic acids
(2) Aryl glyoxylic acid chlorides, R.CO.COCl
(3) Open-chain diketones, R.CO.COR
(4) Ring diketones

The course of the reaction depends upon the reactivity of the aromatic component. The formation of carboxylic acid occurs if the catalyst decomposes the acid chloride before condensation can occur. Arylglyoxylic acids are generally formed with more active aromatic compounds. Open-chain diketones are formed by condensation of highly active aromatic hydrocarbons or ethers with oxalyl chloride in the presence of aluminum chloride.† As the aromaticity, and hence the activity of the aromatic component is increased, however, ring closure may be effected during the condensation. Thus, although biphenyl with oxalyl chloride and aluminum chloride gives a 75 per cent theoretical yield of biphenyl-4-carboxylic acid, as a result of primary decomposition of the acid chloride,[66] 4,4′-dimethylbiphenyl gives a 45-50 per cent yield of 2,7′-dimethylphenanthrene-9,10-quinone [67]:

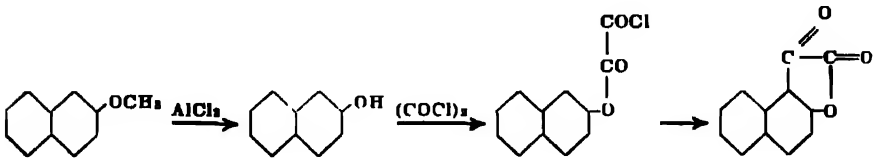


† A more detailed treatment of these reactions is found in Chapter 6.
[66] C. Liebermann and M. Zsuffa, *Ber.*, 44, 852-863 (1911)
[67] C. Liebermann, *Ber.*, 44, 1453-1455 (1911).

The position of the activating group has been found to have a great effect on the course of the reaction. α-Naphthyl methyl ether gives the open-chain diketone,[68]

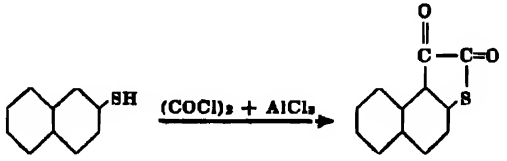


but β-naphthyl methyl ether reacts with primary cleavage of the methoxy-, condensation through the hydroxy- group, and subsequent ring closure to the α-position. β-Naphthofuran-1,2-dione is obtained in 50 per cent yield, probably according to the scheme:



Some ring closure to 1-methoxyacenaphthenequinone also occurs, the amount obtained varying with reaction conditions. The yield of the naphthofurandione decreases with increasing amounts of the acenaphthenequinone obtained, but the best yield of the latter which has been secured is 25 per cent. The ethyl ether of β-naphthol, however, gives only the open diketone, together with traces of lactone or quinone.[69]

β-Naphthol, like its methyl ether, gives a good yield of β-naphthofuran-1,2-dione.[70] β-Thionaphthol similarly gives β-naphthothiofuran-1,2-dione:



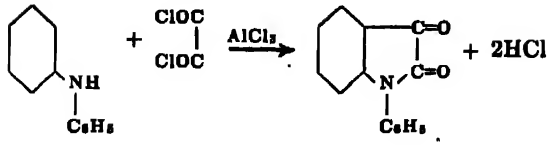
Ring closures occur readily during condensation of N-mono-alkyl- or arylamines with oxalyl chloride, with production of the correspondingly substituted pseudoisatins[71]:

[68] H. Staudinger E. Schlenker, and H. Goldstein, *Helv. Chim. Acta*, 4, 334-342 (1921); *C. A.*, 15, 3445.

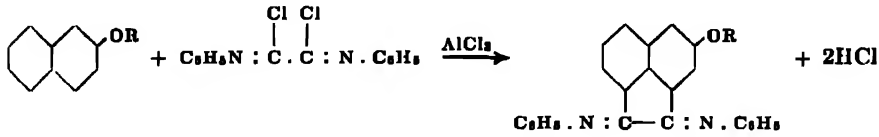
[69] H. Staudinger, E. Schlenker, and H. Goldstein, *loc. cit.*; M. Giua, *Gass. chim. ital.*, 47 (I), 51-57 (1917); *C. A.*, 12, 1169.

[70] M. Giua, *loc. cit.*

[71] R. Stollé, *Ber.*, 46, 3915-3916 (1913); German P. 281,046 (1913) to R. Stollé, *C. A.*, 9, 1999; *C. Z.*, 1915, I, 71.



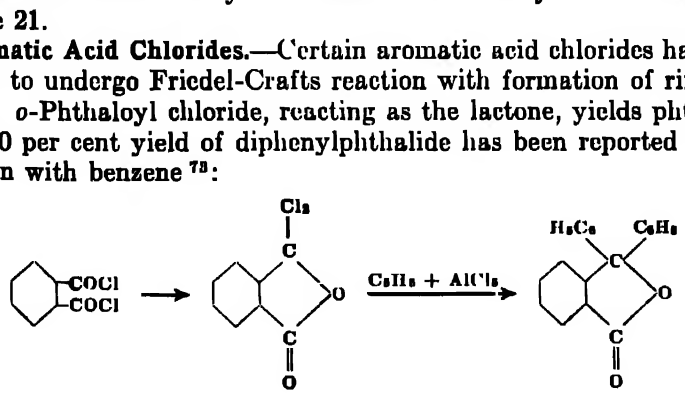
In an attempt to improve yields of quinones, diarylimido- chlorides of oxalic acid have been condensed with aromatic compounds and aluminum chloride. Diphenylimido chloride reacts with naphthalene derivatives to give *peri*-ring closure.[72] Although naphthalene yields only traces of condensation products, the reaction proceeds easily with β-naphthol ethers.



Since the phenylimido- derivatives thus obtained are easily hydrolyzed, the procedure affords a good method for the production of acenaphthenequinones. In this way 2-methoxyacenaphthenequinone was obtained in a 75-77 per cent yield, based on the amount of diphenylimido chloride used. Condensation with β-naphthol occurs through the hydroxy- group, the final product in this case being β-naphthofuran-1,2-dione, obtained in 70 per cent yield. The method showed little promise with anthracene derivatives, N-dialkylarylamines, or benzene derivatives.

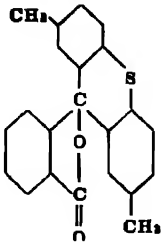
Ring closures effected by condensations with oxalyl chloride are listed in Table 21.

Aromatic Acid Chlorides.—Certain aromatic acid chlorides have been reported to undergo Friedel-Crafts reaction with formation of ring compounds. *o*-Phthaloyl chloride, reacting as the lactone, yields phthalides. An 80-90 per cent yield of diphenylphthalide has been reported by condensation with benzene [73]:



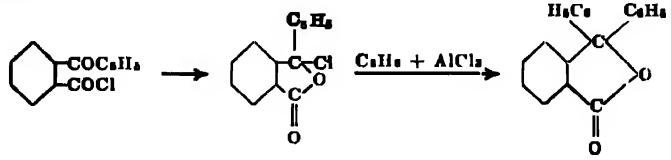
The condensation of *o*-phthaloyl chloride with *m*- and *p*-cresol methyl ethers proceeds analogously.[74] An unusual course, however, is taken in the condensation of *p*-thiocresyl methyl ether with *o*-phthaloyl chloride. The product here is 2',7'-dimethyl-1-thiofluoran, m.p. 228-230°:

[72] H. Staudinger, H. Goldstein, and E. Schlenker, *Helv. Chim. Acta*, 4, 342-364 (1921); *C. A.*, 15, 3446.
[73] A. Baeyer, *Ann.*, 202, 50 (1880).
[74] R. Weiss and W. Knapp, *Monatsh.*, 50, 392-398 (1928); *C. A.*, 23, 1896; *ibid.*, 50, 10-16 (1928), *C. A.*, 22, 3851.



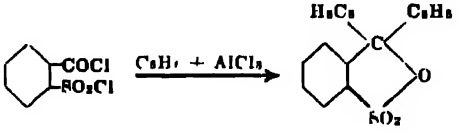
Here replacement of both lactone halogens occurs, but there is also condensation of the thiocresyl residues.

Halides of aromatic keto- acids condense with aromatic hydrocarbons to yield phthalides. *o*-Benzoylbenzoyl chloride yields diphenylphthalide with benzene [75]:

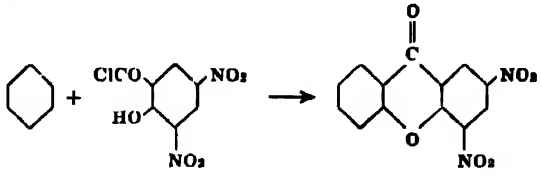


A 90 per cent yield of phenyl-1-naphthylphthalide is thus secured from *o*-1-naphthoylbenzoyl chloride and benzene. Alkylated benzenes or napthalenes react as does benzene in this type of reaction.[76]

o-Sulfobenzoic acid chloride may likewise react as lactone in Friedel-Crafts reaction with benzene [77]:



Condensation of aromatic *o*-hydroxy- acid chlorides with benzene may result in replacement of halogen as well as ring closure, with splitting off of water. Dinitrosalicylyl chloride and benzene thus yield 2,4-dinitroxanthone [78]:



Another condensation involving *ortho*-substituents is that of *o*-chloroselenobenzoyl chloride with benzene, with production of selenoxanthone in good yield.[78]

[75] H. Meyer, *Monatsh.*, 25, 1177-1195 (1904), *J. Chem. Soc. Abs.*, 88 (I), 135 (1905); *ibid*, 25, 471 (1904); 28, 1211 (1907).
[76] E. Clar, *Ber.*, 63, 112-120 (1930); *Brit Chem. Abs.-A*, 334 (1930)
[77] R. List and M. Stern, *Ber.*, 31, 1648-1672 (1898).
[78] F. Ullmann, *Ann.*, 366, 70-118 (1909).

Table 21. Intermolecular Ring Closures with Evolution of HCl

Aromatic Component	Halogenated Component	Product	Yield	Ref
		Hydrocarbon Synthesis		
Benzene	dichloromethane	anthracene		21
Toluene	dichloromethane	three dimethyl-anthracenes		24,51 86-7,88
Toluene	dichloromethane	2-methylanthracene		86
Di-*p*-tolyl-methane	dichloromethane	dimethylanthracenes		90
Benzene	chloroform	anthracene		94,95
Toluene	chloroform	dimethylanthracenes		24,86-7, 96
Toluene	chloroform	2-methylanthracene		86
Benzene	ethylidene chloride	*sym-meso*-dihydro-dimethylanthracene		23
Benzene	acetylene dibromide	anthracene		26
Benzene	trichloroethane	anthracene		91
Benzene	*sym*-tetrabromoethane	anthracene		25,26
Toluene	*sym*-tetrabromoethane	dimethylanthracenes		23-4, 55-6,87
Toluene	*sym*-tetrabromoethane	2-methylanthracene		86
Xylenes	*sym*-tetrabromoethane	tetramethylanthracenes		85
Benzene	perchloroethylene	anthracene		92
Benzene	pentachloroethane	anthracene		92
Benzene	hexachloroethane	anthracene		92
benzene	benzyl chloride	anthracene		72-3,86
Toluene	benzyl chloride	dimethylanthracenes		72,86-7
Benzene	benzal chloride	diphenylanthracenedi-hydride		74
Benzene	α-chloroethyl benzene	*meso*-dimethyldihydro-anthracene		73
Benzene	α,β-dibromoethyl-benzene	anthracene		73
Benzene	allyl chloride	diethyldihydro-anthracene		84
Biphenyl	dichloromethane	fluorene		22

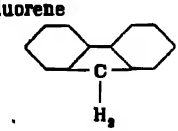


Table 21—*(Continued)*

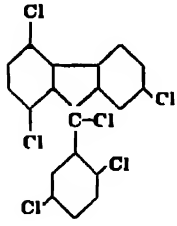
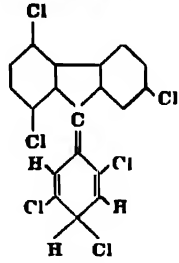
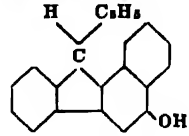
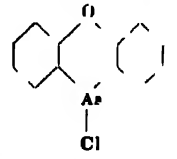
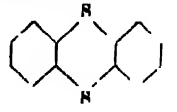
Aromatic Component	Halogenated Component	Product	Yield	Ref
p-dichlorobenzene	carbon tetrachloride	phenylfluorene derivatives (I) and (II)	24%	49
		 (I)		
		 (II)		
Naphthalene	diphenyldichloromethane	9-phenyl-1,2-benzofluorene and 9-phenyl-3,4-benzofluorene		27
α-Naphthol	diphenyldichloromethane	3-hydroxy-9-phenyl-1,2-benzofluorene 	almost theoretical	27
9-Bromophenanthrene	(with itself)	2,3,10,11-dibenzoperylene		28
1-Bromonaphthalene	(with itself)	perylene	4%	53
Benzyl chloride	(with itself)	anthracene	low	72,93
α-Chloroethylbenzene	(with itself)	*meso*-dimethyldihydroanthracene		73
Xylyl chloride ($CH_3 . C_6H_4CH_2 . Cl$)	(with itself)	dimethylanthracenes		72,86-7
Diphenyl ether	arsenic trichloride	5-chlorophenoxarsine 		31
Phenyl α-naphthyl ether	arsenic trichloride	7-chloro-α,β-naphthaphenoxarsine		32
Benzene	sulfur dichloride	thianthrene 		68-9
Toluene	sulfur dichloride	ditolyene disulfide		68

Table 21—*(Continued)*

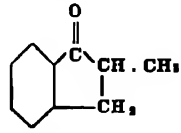
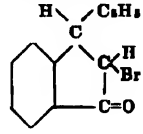
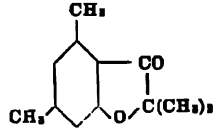
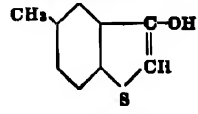
Aromatic Component	Halogenated Component	Product	Yield	Ref.
		Halogenated Aliphatic or Aralkyl Saturated Acid Chlorides		
Benzene	trichloroacetyl chloride	fluorene-2-carboxylic acid		29
Benzene	β-chloropropionyl chloride	1-hydrindone		66
Toluene	β-chloropropionyl chloride	mixture of 4- and 6-methyl-1-hydrindones		66
Chlorobenzene	β-chloropropionyl chloride	4- and 6-chloro-1-hydrindones		66
Benzene	α-bromoisobutyryl bromide	2-methyl-1-hydrindone 		55
Benzene	β-chlorobutyryl chloride	3-methyl-1-hydrindone		66
Chlorobenzene	β-chlorobutyryl chloride	4- and 6-chloro-3-methyl-1-hydrindone		66
Benzene	phenyl-α,β-dibromopropionyl chloride	1-phenyl-2-bromo-3-hydrindone 		8
sym-m-xylenol methyl ether	α-bromopropionyl bromide	1,3,5-trimethylcoumaranone	60-70%	64
sym-m-xylenol methyl ether	α-bromoisobutyryl bromide	1,1,3,5-tetramethylcoumaranone 		62
sym-m-xylenol methyl ether	α-bromobutyryl bromide	1-ethyl-3,5-dimethyl coumaranone		63
sym-m-xylenol methyl ether	α-bromoisovaleryl bromide	1-isopropyl-3,5-dimethylcoumaranone		63
Resorcinol	α-bromovaleryl chloride	5-hydroxy-1-propyl coumaranone		54
p-Thiocresol methyl ether	chloroacetyl chloride	5-methyl-3-hydroxythianaphthene 	50%	44

Table 21—*(Continued)*

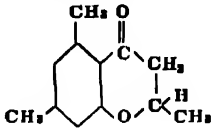
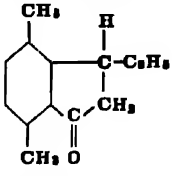
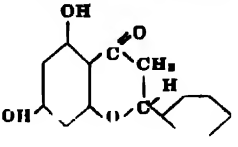
Aromatic Component	Halogenated Component	Product	Yield	Ref
β-naphthyl methyl sulfide	chloroacetyl chloride	4,5-benzo-3-hydroxythianaphthene	very low	70,71
β-Naphthyl methyl sulfide	β-bromopropionyl chloride	5,6-benzothiochromanone	traces	70,71
	Unsaturated Aliphatic or Aralkyl Acid Chlorides			
Chlorobenzene	crotonyl chloride	4- and 6-chloro-3-methyl-1-hydrindone		66
m-Dichlorobenzene	crotonyl chloride	4,6-dichloro-3-methyl-1-hydrindone		66
p-Xylene	crotonyl chloride	3,4,7-trimethyl-1-hydrindone (with the acyl derivative)		7
p-Cresyl methyl ether	crotonyl chloride	2,6-dimethylchromanone and 3,4-dimethyl-7-hydroxyhydrindone as by-product		33
sym-m-Xylenyl methyl ether	crotonyl chloride	2,5,7-trimethylchromanone 		63
p-Tolylmethyl ether	α-ethylcrotonyl chloride	dimethylethylchromanone	low	65
sym-m-Xylenyl methyl ether	β,β-dimethylacrylyl chloride	2,2,5,7-tetramethylchromanone		63
p-Cresyl methyl ether	β,β-dimethylacrylyl chloride	2,2,6-trimethylchromanone		33
o- or *m*-Xylene	cinnamoyl chloride	no hydrindone		7,8
p-Xylene	cinnamoyl chloride	4,7-dimethyl-3-phenyl-1-hydrindone 		7
Phloroglucinol	cinnamoyl chloride	5,7-dihydroxyflavanone 		38,39
Phloroglucinol	*p*-carbethoxycinnamoyl chloride	5,7,4′-trihydroxyflavanone		38,39

Table 21—*(Continued)*

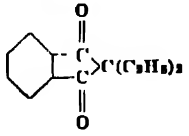
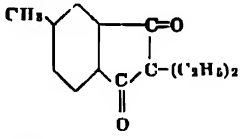
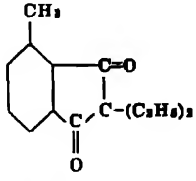
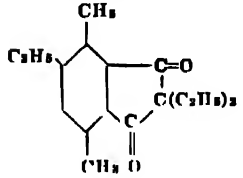
Aromatic Component	Halogenated Component	Product	Yield	Ref.
Phloroglucinol	*o*-methoxycinnamoyl chloride	5,7-dihydroxy-2'-methoxyflavanone		38,39
		Malonyl Halides		
Benzene	dimethylmalonyl chloride	no indandione		2
Benzene	diethylmalonyl chloride	2,2-diethylindan-1,3-dione (72 g from 59.1 g chloride and 24 g benzene—note 79) 		1,79
Benzene	dipropylmalonyl chloride	2,2-dipropylindan-1,3-dione		2
Toluene	diethylmalonyl chloride	two indandiones (total of 58 g from 118.2 g chloride and 55.2 g toluene) together with an acyclic ketone  and 		40
1,4-Dimethyl-2-ethylbenzene	diethylmalonyl chloride	5-ethyl-4,7-dimethyl-2,2-diethylindan-1,3-dione (38.8 g from 26.8 g hydrocarbon) 		78

Table 21—*(Continued)*

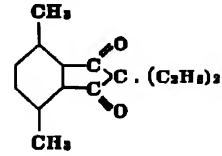
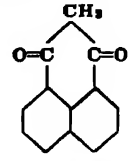
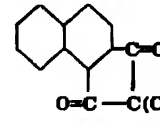
Aromatic Component	Halogenated Component	Product	Yield	Ref.
p-Xylene	diethylmalonyl chloride	4,7-dimethyl-2,2-diethylindan-1,3-dione 		77,79
m-Xylene	diethylmalonyl chloride	4,6-dimethyl-2-diethylindan-1,3-dione		77
p-Cymene	dimethylmalonyl chloride	cymyldimethylindandione		1
p-Cymene	diethylmalonyl chloride	2,2,4-trimethyl-7-isopropylindan-1,3-dione (72 g from 53.6 g *p*-cymene and 78.8 g. chloride)		2,40
p-Cymene	dipropylmalonyl chloride	4-methyl-2,2-dipropyl-7-isopropylindan-1,3-dione		2
Naphthalene	malonyl chloride or bromide	1,3-*peri*-naphthindandione 		13,14
peri-Naphthindandione	malonyl bromide	pyrene(upon reduction)		14
Naphthalene	dimethylmalonyl chloride	three isomeric dimethylindandiones		2
Naphthalene	diethylmalonyl chloride	three isomeric diethylindandiones		1,16
Naphthalene	dipropylmalonyl chloride	no definite condensation products		2
Ethylnaphthalene	diethylmalonyl chloride	2,2-diethyl-α,β-naphthindandione-1,3 		15
α-Methylnaphthalene	diethylmalonyl chloride	α-methylnaphthdiethylindandiones, oil, b. 250°/13 mm		40
β-Methylnaphthalene	diethylmalonyl chloride	β-methylnaphthdiethylindandiones, oil, b. 230-240°/15 mm		40

Table 21—*(Continued)*

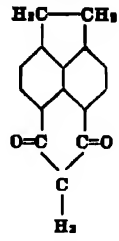
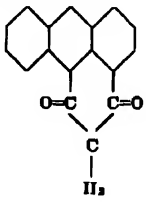
Aromatic Component	Halogenated Component	Product	Yield	Ref.
Acenaphthene	malonyl bromide	*peri*-acenaphthene-indandione 		67
Acenaphthene	dimethylmalonyl chloride	two isomeric dimethyl-acenaphtheneindandiones		2
Acenaphthene	diethylmalonyl chloride	two isomeric diethyl-acenaphtheneindandiones		1
Anthracene	malonyl chloride	anthracene-1,9-indandione 		20
Anthracene	dimethylmalonyl chloride	one dimethylanthraceneindandione		2
Anthracene	diethylmalonyl chloride	one diethylanthraceneindandione		1
Phenanthrene	dimethylmalonyl chloride	one dimethylphenanthreneindandione		2
Phenanthrene	diethylmalonyl chloride	one diethylphenanthreneindandione		1
Retene	dimethylmalonyl chloride	one dimethylretene-indandione		2
Retene	diethylmalonyl chloride	one diethylretene-indandione		1
Biphenyl	dipropylmalonyl chloride	dipropylbiphenyl-indandione		2
Fluorene	dimethylmalonyl chloride	two dimethylfluorene-indandiones and isobutylfluorene		79
p-Tolyl methyl ether	malonyl chloride	4-hydroxy-7-methyl-indan-1,3-dione	50%	75
p-Tolyl methyl ether	ethylmalonyl chloride	4-hydroxy-7-methyl-2-ethylindan-1,3-dione		75

Table 21—*(Continued)*

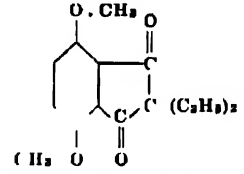
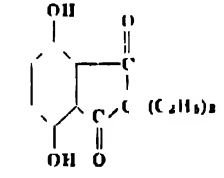
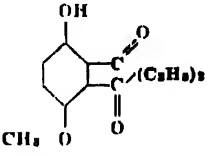
Aromatic Component	Halogenated Component	Product	Yield	Ref
p-Tolyl methyl ether	diethylmalonyl chloride	4-hydroxy-7-methyl-2,2-diethylindan-1,3-dione		75
p-Tolyl methyl ether	*n*-propylmalonyl chloride	4-hydroxy-7-methyl-2-*n*-propylindan-1,3-dione	100%	75
p-Tolyl methyl ether	*n*-butylmalonyl chloride	4-hydroxy-7-methyl-2-*n*-butylindan-1,3-dione	100%	75
Anisole	dimethylmalonyl chloride	no indandione obtained		40
Veratrole	dimethylmalonyl chloride	three indandiones (isomeric and methoxy cleavage products)		40
Veratrole	diethylmalonyl chloride	four indandiones (isomeric and methoxy cleavage products)		34
Hydroquinone dimethyl ether	diethylmalonyl chloride	(I) 4,7-dimethoxy-2,2-diethylindan-1,3-dione  (II) 4,7-dihydroxy-2,2-diethylindan-1,3-dione  (III) 4-hydroxy-7-methoxy-2,2-diethylindan-1,3-dione 		34
Resorcinol dimethyl ether	dimethyl- or diethylmalonyl chloride	no indandiones obtained		34,40
Resorcinol dimethyl ether	malonyl chloride	4-hydroxy-6-methoxyindan-1,3-dione	30%	76

Table 21—*(Continued)*

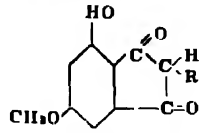
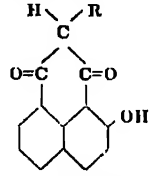
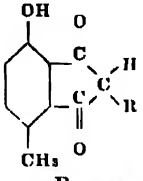
Aromatic Component	Halogenated Component	Product	Yield	Ref.
Resorcinol dimethyl ether	methyl-, ethyl-, *n*-propyl-, or *n*-butylmalonyl chloride	4-hydroxy-6-methoxy-2-alkyl-indan-1,3-dione (resinous) 		76
		R = methyl	—	
		= ethyl	62%	
		= *n*-propyl	84%	
		= *n*-butyl	62%	
β-Naphthyl methyl ether	malonyl chloride	4-hydroxy-*peri*-naphthindan-1,3-dione	31%	76
β-Naphthyl methyl ether	ethyl-, propyl-, or butylmalonyl chloride	4-hydroxy-2-alkyl-*peri*-naphthindan-1,3-dione (resinous) 		76
		R = ethyl	50%	
		= *n*-propyl	95%	
		= *n*-butyl	75%	
p-Cresol	methylmalonyl chloride	4-hydroxy-2,7-dimethylindan-1,3-dione		75
p-Cresol	butylmalonyl chloride	4-hydroxy-7-methyl-2-*n*-butylindan-1,3-dione	85%	75
p-Cresol	amyl-, hexyl-, heptyl-, isopropyl-, isobutyl-, or isoamylmalonyl chloride	4-hydroxy-7-methyl-2-alkylindan-1,3-dione 		75
		R = *n*-amyl	29%	
		= *n*-hexyl	31%	
		= *n*-heptyl	50%	
		= isopropyl	16%	
		= isobutyl	47%	
		= isoamyl	44%	
p-Tolyl acetate	*n*-butylmalonyl chloride	4-hydroxy-7-methyl-2-*n*-butylindan-1,3-dione	100%	75

Table 21—*(Continued)*

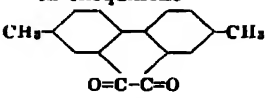
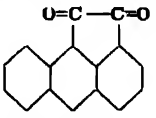
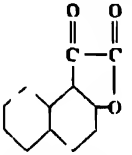
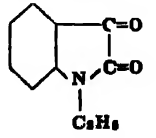
Aromatic Component	Halogenated Component	Product	Yield	Ref
		Oxalyl Chloride		
Biphenyl	oxalyl chloride	no ring closure		17,80
4,4'-Dimethyl biphenyl	oxalyl chloride	*p,p'*-dimethylphenanthrenequinone 	45–50%	17
Anthracene	oxalyl chloride	acenanthraquinone 		18,19
2-methoxynaphthalene	oxalyl chloride	β-naphthafuran-1,2-dione (50% yield—note 35)  and 1-methoxyacenaphthenequinone (traces to 25% yields —note 35)		35,41, 37
2-Ethoxynapthalene	oxalyl chloride	1,1'-diethoxy-4,4'-binaphthoyl (69%) and traces of 1-ethoxyacenaphthenequinone (note 35) or traces of lactone (note 36)		35,36
2,7-Dimethoxynaphthalene	oxalyl chloride	7-methoxy-β-naphthofuran-1,2-dione and small amount of 2,7-dimethoxyacenaphthenequinone	45%	35
β-Naphthol	oxalyl chloride	β-naphthafuran-1,2-dione	good	36,42
β-Thionaphthol	oxalyl chloride	β-naphthathiofuran-1,2-dione		42
α-Naphthol	oxalyl chloride	6,7-benzocoumaran-2,3-dione	small	37
N-Mono-alkyl or aryl derivatives of aromatic amines, *e.g.*, N-Ethylaniline or N-phenylaniline	oxalyl chloride	N-alkyl or aryl substituted pseudoisatins; *e. g.*, N-ethylpseudoisatin 		46,47

Table 21—*(Continued)*

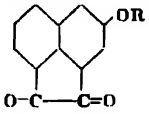
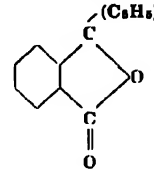
Aromatic Component	Halogenated Component	Product	Yield	Ref.
Diphenylamine	oxalyl chloride	acridine carboxylic acid		81
Benzylidene-phenylhydrazine	oxalyl chloride	1-benzylideneamino-pseudoisatin		82
β-N-Ethylamino-naphthalene	oxalyl chloride	β-ethylnaphthindol-1, 2-dione		42
N-Monoaryl-aminoanthra-quinones	oxalyl chloride	N-anthraquinonyl-pseudoisatins		48
Methyl or ethyl β-naphthyl ether	diphenylimido chloride	2-alkoxyarenaphthene-quinone  R = methyl = ethyl	75% 44%	30
Methyl β-naphthyl ether	di-*o*-tolyloxamidyl chloride	1-alkoxyacenaphthene-quinone	62%	30
		Aromatic Acid Chlorides		
Benzene	*o*-phthaloyl chloride	diphenylphthalide (note 4 and 57) 	80–90% (note 4)	4,57
		also: diphenylanthrone phenyloxanthranol *o*-benzoylbenzoic acid tetraphenylmethane *o*-carboxylic acid		58,61
Toluene	*o*-phthaloyl chloride	ditolylphthalide	theoretical	5
p-Thiocresyl methyl ether	*o*-phthaloyl chloride	2′,7′-dimethyl-1-thio-fluoran		45
Methyl ether of *p*-bromothio-phenol	*o*-phthaloyl chloride	2′,7′-dibromo-1-thio-fluoran		43
Benzene	*o*-benzoylbenzoyl chloride	diphenylphthalide		50
2-Methyl naphthalene	*o*-benzoylbenzoyl chloride	phenyl-2-methyl-1-naphthylphthalide		52
1-Methyl-naphthalene	*o*-benzoylbenzoyl chloride	phenyl-4-methyl-1-naphthylphthalide		52

Table 21—*(Continued)*

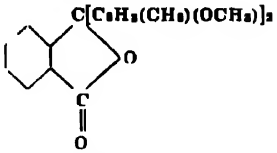
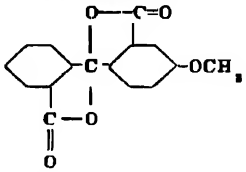
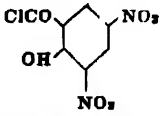
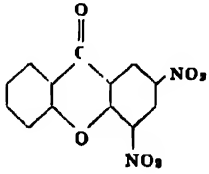
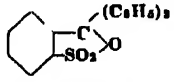
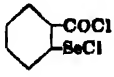
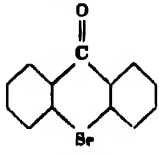
Aromatic Component	Halogenated Component	Product	Yield	Ref
m-Cresyl methyl ether	*o*-phthaloyl chloride	*m*-cresolphthaleindimethyl ether 	80%	83
m-Methoxy benzoic acid	*o*-phthaloyl chloride	4'-methoxybenzophenone-2,2'-dicarboxylic acid dilactone 	40%	83
p-Cresyl methyl ether	*o*-phthaloyl chloride	*p*-cresolphthalein dimethyl ether	60%	45
p-bromomethoxybenzene	*o*-phthaloyl chloride	*p*-bromophenolphthalein dimethyl ether	60%	43
Benzene	*o*-1-naphthoylbenzoyl chloride	phenyl-1-naphthylphthalide	90%	52
Toluene	*o*-1-naphthoylbenzoyl chloride	*p*-tolyl-1-naphthylphthalide		52
m-Xylene	*o*-1-naphthoylbenzoyl chloride	*m*-xylyl-1-naphthylphthalide	50–55%	52
Benzene	3,5-dinitro-6-hydroxybenzoylchloride 	2,4-dinitroxanthone 		9
Benzene	*o*-sulfobenzoic acid chloride (as lactone) 			10,11
Benzene	*o*-chloroselenobenzoyl chloride 	selenoxanthone (7.5 g from 10 g acid chloride) 		12

Table 21—*(Continued)*

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Chapter 8

Addition Reactions. Part I

Aluminum chloride is an active agent in promoting the addition of aromatic compounds to olefinic double bonds. The study of such reactions comprises the bulk of this chapter.

The alkylation of aromatic compounds by straight-chain or cycloölefin hydrocarbons in the presence of aluminum chloride is an important industrial reaction and has been applied quite extensively. Such reactions are not limited to hydrocarbons, however; analogous reactions are found in which aromatic compounds add to acids, esters, ketones, and acid chlorides having an olefinic bond.

An interesting phenomenon is shown in the reversibility of reactions involving the addition of an aryl group to compounds having conjugated double bonds.

Arylcycloölefins may isomerize in the presence of aluminum chloride to give higher ring structures. This type of intramolecular addition has been particularly important in the synthesis of polynuclear hydrocarbons for use in the study of carcinogenic compounds.

Other addition reactions covered in this chapter include a study of the products obtained on reacting arylglycolic acids or arylglyoxals with aromatic compounds, and the opening of lactone and phthalide rings upon addition with aromatic hydrocarbons. The reactions of acetylene in the presence of aluminum chloride are also noted.

Although the reaction between aromatic and paraffinic hydrocarbons is not a true addition reaction because of apparent scission of the paraffin chain, the character of the products indicates that alkylation is the main reaction. Similarly, cycloparaffins readily open up to form alkylating agents.

A group of miscellaneous reactions concludes this chapter. These include the addition reactions of alkylene oxides, additions to a cyanogen group, either as cyanogen itself or as a nitrile, reactions of benzoyl peroxide, and finally the products obtained by adding carbon dioxide or sulfur dioxide to aromatic compounds in the presence of aluminum chloride.

The addition of di- or polycarboxylic acid anhydrides to aromatic or heterocyclic compounds, resulting in the production of keto- acids, has been so extensively studied that it has been deemed advisable to devote a separate chapter to this reaction.*

*See Chapter 9.

Addition of Aromatic Hydrocarbons or their Derivatives to Compounds with Double Bonds

Reaction of olefins with aromatic hydrocarbons occurs with addition of the hydrocarbon at the olefinic double bond. With ethylene it proceeds according to the scheme:

$$CH_2 : CH_2 + C_6H_6 \xrightarrow{AlCl_3} CH_3 . CH_2 . C_6H_5$$

The addition seems to be general for aliphatic hydrocarbons. Benzene homologs, polynuclear hydrocarbons, phenols, and phenol ethers add even more readily. The reaction has been extended to addition of aliphatic or alicyclic compounds at the olefinic linkage *

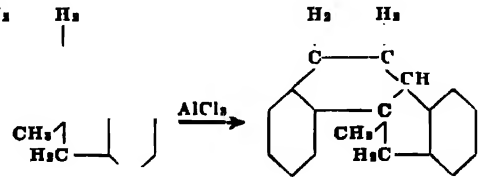
Aromatic hydrocarbons add to the double bond of unsaturated acids or esters,

$$C_6H_5CH : CHCOOH \xrightarrow{C_6H_6 + AlCl_3} (C_6H_5)_2CHCH_2COOH$$

and to unsaturated ketones,

$$CH_3CO\ CH : C(CH_3) \xrightarrow{C_6H_6 + AlCl_3} CH_3CO . CH_2 . C(CH_3)(C_6H_5)$$

Intramolecular ring closures may be effected through addition at double bonds,



In ketone synthesis with unsaturated acid chlorides, not only condensation with cleavage of hydrogen chloride occurs, but also addition of the aromatic hydrocarbons at the double bond, or ring closure through addition at the double bond.†

The mechanism of the addition of aromatic hydrocarbons to compounds with olefinic double bonds has been assumed by various investigators to proceed through intermediate addition of hydrogen chloride (formed by the action of water on aluminum chloride) at the double bond, and subsequent condensation of the halogenated saturated product with the aromatic component. Balsohn [1] points out that in the reaction of ethylene with benzene, evolution of hydrogen chloride is noted only for a short time. He assumed that the initially freed hydrogen chloride was due to the action of moisture on aluminum chloride. This harmo-

* See section on Friedel-Crafts reaction in aliphatic chemistry, Chapter 17.
† See pages 212, 242 and 248.

nizes with the theory which has been advanced by Grosse and Ipatieff.[2] They state that the following cycle of reactions probably occurs during reaction:

$$CH_2{:}CH_2 + HCl \longrightarrow CH_3CH_2Cl$$
$$C_6H_6 + CH_3CH_2Cl \longrightarrow C_6H_5.CH_2.CH.CH_3 + HCl$$
$$CH_2{:}CH_2 + HCl \longrightarrow CH_3CH_2Cl$$

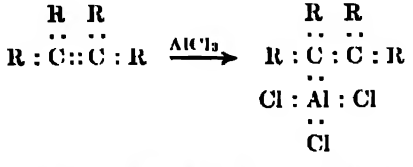
According to this scheme, evolution of hydrogen chloride would be noted only upon contact of the catalyst with moisture; since the gas evolved as a consequence of subsequent Friedel-Crafts condensation would be consumed by addition to the ethylene present, its evolution would not be apparent during the course of the reaction. Grosse and Ipatieff found that reaction is initiated by addition of hydrogen chloride to the reaction mixture; when much hydrogen chloride was used, ethyl chloride was detected in the product. The advantageous use of hydrogen chloride for initiating reaction between an unsaturated compound and benzene is often cited in the literature,[3] and has been borne out in the author's laboratory.

Ipatieff and his co-workers later [4] suggest that reaction may occur through formation of the yet unknown hydrogen aluminum tetrachloride from hydrogen chloride and the catalyst and subsequent reaction with olefins to yield alkyltetrachloroaluminates, which are the active agents in Friedel-Crafts alkylations with olefins:

$$AlCl_3 + HCl \longrightarrow HAlCl_4$$
$$RCH{:}CH_2 + HAlCl_4 \longrightarrow \underset{\displaystyle ClAlCl_3}{RCH.CH_3}$$

Since isomerization of alkyl tetrachloroaluminates is said to occur slowly, if at all, reaction with benzene proceeds without branching.[5]

According to Nenitzescu,[6] the accelerating effect of hydrogen chloride on alkylations effected with aluminum chloride is possibly due to the fact that the solubility of aluminum chloride is thereby increased. Olefins have an extraordinarily great affinity for aluminum chloride forming a complex with it probably according to the scheme:



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[5] *cf.* L. I. Smith and W. W. Prichard, *J. Am. Chem. Soc.*, 62, 770-7 (1940) concerning rearrangement with unsaturated acids.
[6] C. D. Nenitzescu, *Angew. Chem.*, 52, 231 (1939). C. D. Nenitzescu, Personal communication.

The resulting complex contains a carbon atom which has only six electrons and is therefore unstable. When no addendum is present, polymerization occurs.[7] When a reactant component is present, addition occurs. Such a theory has also been advanced to explain the catalytic activity of boron fluoride in alkylations.[8] It is suggested that the common factor in the so-called Friedel-Crafts type catalysts is the electron-deficient nature of the catalyst, and that such catalysts may associate with the electrons of the carbon-carbon double bond to give an active intermediate common to each reaction.

On the other hand, other investigators assume that Friedel-Crafts alkylation occurs primarily through addition of the aromatic component at the olefinic double bond. As early as 1885, Essner and Gossin[9] suggested that the hydrogen chloride evolved in the reaction of amyl chloride with benzene was due to dehydrohalogenation of the alkyl halide by the catalyst, and that alkylation occurred through addition of benzene to the resulting olefin. In studying the mechanism of the addition of aromatic hydrocarbons to unsaturated carboxylic acids, Eijkman[10] noted that the hydrohalogenated products of several unsaturated acids did not condense with benzene in presence of aluminum chloride, thus:

$$(CH_3)_2CH \cdot CHBrCOOH \xrightarrow{C_6H_6 + AlCl_3} \text{no reaction}$$

$$(CH_3)_2C : CHCOOH \xrightarrow{C_6H_6 + AlCl_3} (CH_3)_2CH \cdot CH(C_6H_5)COOH$$

Therefore, according to Eijkman, the assumption that the addition of aromatic hydrocarbons to unsaturated acids in the presence of aluminum chloride depends upon a primary formation of hydrogen chloride addition products, is not a sufficient explanation of the reaction. Böeseken[11] has also pointed out that the majority of catalysts possess residual valences, and that they may be described as "open" systems, whereas the majority of organic substances, even unsaturated compounds, are "closed." When the two are brought together into contact, the closed system is partly opened, yielding an activated molecule. From a long series of studies of Friedel-Crafts reactions effected with aromatic hydrocarbons and various aliphatic, arylalkyl, and inorganic chlorides in presence of aluminum chloride, Böeseken[12] concluded that the Friedel-Crafts reaction proceeds by a dissociating action of the catalyst on the chloride, the catalyst acting only by decomposing the chloride into an active constituent. He concluded that, in order to secure condensation, an unsaturated compound and one which can be so activated that it can combine

[7] *cf.* F. C. Whitmore, *Ind. Eng. Chem.*, 26, 94-95 (1934). C. D. Nenitzescu and C. N. Ionescu, *Ann.*, 491, 189 (1931).

[8] C. C. Price and M. Meister, *J. Am. Chem. Soc.*, 61, 1595-1597 (1939). C. C. Price and J. M. Cukowski, *J. Am. Chem. Soc.*, 60, 2499-2502 (1938).

[9] J. C. Essner and E. Gossin, *Bull. soc. chim.*, 42, 213-216 (1884); *J. Chem. Soc. Abs.*, 48, 517 (1885).

[10] J. F. Eijkman, *Chem. Weekblad*, 5, 655-666; *C. Z.*, 1908, II, 1100.

[11] J. Böeseken, *Rec. trav. chim.*, 45, 453-474 (1926); *Brit. Chem. Abs.-A*, 806 (1926).

[12] J. Böeseken, *loc. cit.*; *Rec. trav. chim.*, 24, 6-18 (1905); 29, 85-113 (1910), 30, 148-150, 381-391 (1911); 33, 196-203 (1914). For the proton theory advanced by the author, see Chapter 4.

with the unsaturated compound must be brought together in the presence of a catalyzer, the reaction being made possible by a loss of free energy. On the basis of his assumptions, the necessity for the varying proportions of aluminum chloride required for different types of Friedel-Crafts reactions may be explained by the varying ease with which the halogenated constituent is decomposed. Ketone synthesis with acid halides thus requires the use of at least one mole of $AlCl_3$, whereas alkylation with the more easily dissociated alkyl halides or with olefins requires only catalytic amounts.

Reaction of Olefinic Hydrocarbons with Aromatic Hydrocarbons

In 1879, Balsohn [13] reported that upon passing a mixture of dry ethylene and hydrogen chloride gas into a mixture of benzene and aluminum chloride, the ethylene is absorbed, and a liquid is obtained which has the properties of ethylbenzene. If ethylene alone is passed into the same mixture, hydrogen chloride evolution is noted only for a short time, absorption of ethylene continuing long after hydrogen chloride evolution had ceased. The product consisted of a mixture of mono- and polyethylated benzenes.

A few years later Istrati [14] noted that various nuclearly ethylated chlorobenzenes are formed by passing ethylene into a mixture of aluminum chloride and chlorobenzene.

The reaction was applied by Gattermann and his co-workers [15] to the formation of 1,3,5-triethylbenzene from benzene and ethylene, 1,3,5-methyldiethylbenzene from toluene and ethylene, and 1,3,5-dimethylethylbenzene from ethylene and xylene.

Schleicher and Buttgenbach [16] have secured 66 g of triethylbenzene by passing ethylene for fourteen hours into a mixture of 50 g of benzene and 60 g of aluminum chloride. When passage of ethylene was stopped after ten hours, 42 g of hexaethylbenzene was secured.

Optimum conditions for the ethylation of aromatic hydrocarbons in the presence of aluminum chloride have been studied. High-speed stirring is effective in inducing complete reaction of ethylene with benzene at 70-90°.[17] Berry and Reid [18] have made a comprehensive study of the reaction. For the ethylation of benzene, 1 mole of aluminum chloride to about 13 moles of benzene was found to be the best ratio. Results obtained by using 0.20-5.74 moles of ethylene per mole of benzene show that the yield of ethylbenzene increases regularly to about 30 per cent when about 1.1 moles of ethylene have been passed in, that the yield of di- and triethylbenzenes never goes much above 20 per cent, that pentaethylbenzene is present almost from the first in a remarkably low and

[13] M. Balsohn, *Bull. soc. chim. (2)*, 31, 538-542 (1879); *J. Chem. Soc. Abs.*, 786 (1879).
[14] C. I. Istrati, *Bull. soc. chim.*, 42, 111-116; *J. Chem. Soc. Abs.*, 48, 251 (1885); *Ann. chim. phys. (6)*, 6, 395-433; *J. Chem. Soc. Abs.*, 50, 220 (1886).
[15] L. Gattermann, S. Frits, and K. Beck, *Ber.*, 32, 1122-1127 (1899).
[16] A. Schleicher and E. Buttgenbach, *J. prakt. Chem.*, 105, 355-360 (1923); *C. Z.*, 1923, III, 825.
[17] C. H. Milligan and E. E. Reid, *J. Am. Chem. Soc.*, 44, 206-210 (1922). C. H. Milligan and E. E. Reid, *Ind. Eng. Chem.*, 15, 1043-1049 (1923); *C. A.*, 17, 3729. See also Chapter 14.
[18] T. M. Berry and E. E. Reid, *J. Am. Chem. Soc.*, 49, 3142-3149 (1927); *C. A.*, 22, 394.

nearly constant concentration to the end, and that hexaethylbenzene appears early and always exceeds the concentration of tetra- or penta-ethylbenzenes. As the amount of ethylene passed in increases, there seems to be preferential formation of triethylbenzene; when somewhat over 3 moles of ethylene have reacted, it constitutes over 50 per cent of the mixture. With 5.74 moles of ethylene, 90.6 per cent of the product is hexaethylbenzene. Toluene was found to be more readily ethylated than benzene, and bromobenzene less so. In alkylation with propylene, it was found that this olefin is taken up by benzene under the same conditions as ethylene, but only about 4 per cent as rapidly; toluene is more readily propylated than benzene, the chief product seeming to be *p*-cymene.

Cline and Reid [19] have worked out a process in which practically all benzene used in ethylation of benzene is converted into monoethylbenzene. Higher ethylated benzenes are de-ethylated by returning them to the reaction mixture, a transfer of ethyl groups occurring

Separation of the diethylbenzenes obtained upon reaction of ethylene with benzene and aluminum chloride reveals that the *m*-isomer is the major constituent.[20] Separation of the isomeric *m*-, *p*-, and *o*-diethylbenzenes was effected by partial sulfonation and fractional crystallization of the barium salt of the diethylbenzene sulfonic acids Advantage was taken of the fact that the *meta*- isomer is more easily sulfonated than the other two isomers. The isolation of *sym*-triethylbenzene from the proper fraction of the ethylation mixture has recently [21] been effected by a similar procedure.

According to Natelson,[22] ethylbenzene is best prepared by first saturating the benzene-aluminum chloride suspension with hydrogen chloride, then introducing ethylene with good stirring at 1 atmosphere of pressure and at below 75°. Grosse and Ipatieff [23] have investigated the use of various catalysts for ethylation of benzene in presence of hydrogen chloride. The following moles of ethylene were found to react at the stated temperature in an autoclave in presence of the indicated catalyst:

Catalyst	Temp (°C)	Moles of Ethylene Converted per Mole of Catalyst
$BeCl_2$	200	50
BF_3	25	35
$AlCl_3$	75	75
$TiCl_4$	170	5
$ZrCl_4$	100	90
$CbCl_5$	75	25
$TaCl_5$	75	60

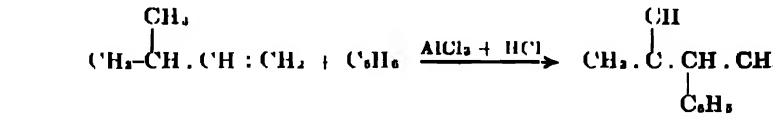
In order to prepare fairly high yields of hexaethylbenzene, Koch and Steinbrink [24] carried out the reaction under pressure. Benzene and aluminum chloride in the molecular proportion of 1.5:1 were placed in a

[19] E. L. Cline and E E Reid, *J Am Chem. Soc*, 49, 3150-3151 (1927)
[20] J. E. Copenhaver and E E Reid, *J Am Chem Soc*, 49, 3157-3164 (1927).
[21] W. B Dillingham and E E Reid, *J Am Chem. Soc*, 50, 2606 (1928); *C. A.*, 33, 150
[22] S. Natelson, *Ind. Eng Chem*, 25, 1291-1296 (1933); *C. A.*, 28, 1668
[23] A V Grosse and V N Ipatieff, *J Org Chem.*, 1, 559-566 (1937); *Brit. Chem Abs*-A (II) 239 (1937)
[24] H. Koch and H. Steinbrink, *Brennstoff-Chemie*, 19, 277-283 (1938).

bomb of such size that the reactants filled one-fourth to one-third of the free space. Ethylene was forced into a pressure of 86 atmospheres, and the reaction brought the temperature to about 85°. The flow of ethylene was continued until no drop in pressure occurred. The yield of hexaethylbenzene obtained was from 56-59 per cent of theoretical. According to Stanley [25] hexaethylbenzene is secured in good yield from the products of the action of ethylene under 50 atmospheres' pressure on benzene in presence of aluminum chloride at room temperature.

In the reaction of higher olefins with benzene and aluminum chloride, cleavage of the olefins may precede alkylation. Thus benzene and diisobutene yield *tert*-butylbenzene and *di-tert*-butylbenzene. Similar results are secured with *n*-butene dimer.[26]

Alkylation by olefins is not generally accompanied by isomerization. Thus isopropylethylene reacts with benzene to yield 2-methyl-3-phenylbutane and not *tert*-amylbenzene [27]:



Cracked gasolines or kerosenes may be used to supply olefinic constituents for production of alkylated benzenes. The influence of the concentration of olefins, the amount of catalyst, the reaction temperature, and the method of addition of catalyst have been studied by Tilicheev and Kuruindin.[28] Optimum conditions were found to comprise the use of about 0.1 mole of aluminum chloride to 1 mole of olefin at 25-30° with 9-10 moles of benzene. The catalyst was added to the benzene in one portion and the olefinic fraction was gradually added to the resulting suspension. Aluminum chloride was compared to aluminum bromide as catalyst for the reaction. With aluminum chloride, an "incubation period" was observed, whereas aluminum bromide caused immediate reaction; this may be traced to the greater solubility of the bromide in benzene. The tar-like layer formed during the reaction from aluminum chloride and the hydrocarbons loses none of its activity during the course of reaction; it may be used as catalyst for a new condensation. The reaction was postulated as proceeding through the series of reactions:

$$R.CH{:}CH_2 + HX \longrightarrow R.CHX.CH_3$$
$$RCHX.CH_3 + C_6H_6 \longrightarrow R.CH(C_6H_5).CH_3 + HX$$

The average yield of benzene homologs amounted to 60 per cent; in some cases 76 per cent yields were secured. In order to investigate the behavior of branched-chain olefins, diamylene was prepared and condensed with benzene. Here the main product consisted of a mixture of benzene

[25] H. M. Stanley, *J. Soc. Chem. Ind.*, 49, 349T-354 (1930).
[26] V. N. Ipatieff and H. Pines, *J. Am. Chem. Soc.*, 58, 1056 (1936); *C. A.*, 30, 519.
[27] V. N. Ipatieff, H. Pines, and L. Schmerling, *J. Org. Chem.*, 5, 253-263 (1940).
[28] M. D. Tilicheev and K. S. Kuruindin, *Neftyanoe Khoz.*, 19, 550-593 (1930); *C. A.*, 25, 3469; *C. Z.*, 1931, I, 2569-2561.

homologs with short chains. Obviously cleavage of the olefin had occurred. From the cracked benzine fractions the following alkyl benzenes were secured: amyl-, *tert*-amyl-, hexyl-, heptyl-, octyl-, nonyldecyl-, undecyl-, and cetylbenzene. The solubility of the alkyl benzenes in 98 per cent sulfuric acid was found to decrease with increasing molecular weight; since the higher homologs were much more difficult to sulfonate than the lower ones, isolation could not be effected through their sulfonates. The following results are reported:

b.p. (°C)	% Olefin	-benzene	b.p (°C)	*D*	*N*	% Yield
30-40	45.0	amyl		$\frac{23.5}{4}$ 0.8576	$\frac{17\ 9}{D}$ 1.4850	69 3
65-68	49.8	hexyl	219-223	$\frac{23.5}{4}$ 0.8581	$\frac{17.9}{D}$ 1.4860	76
95-98	50 4	heptyl	229-231	$\frac{21.5}{4}$ 0.8598	$\frac{18.5}{D}$ 1.4857	68
120-127	48.1	octyl	115 5-118.5 at 9 mm	$\frac{20.5}{4}$ 0.8593	$\frac{18\ 4}{D}$ 1.4861	72
145-150	52.0	nonyl	145-147 at 19 mm	$\frac{22}{4}$ 0.8616	....	58
168-170	49.8	decyl	131-132 at 3 mm	$\frac{22}{4}$ 0 8623	$\frac{22}{D}$ 1.4856	62
195-196	48 3	undecyl	142-146 at 6 mm	$\frac{23.5}{4}$ 0.8572	$\frac{18\ 7}{D}$ 1 4829	44
139-139 at 5 mm	28.8	cetyl	191-194 at 3 mm	$\frac{20.5}{4}$ 0.8640	$\frac{18\ 8}{D}$ 1.4839	48

Ethylene may be separated from gases containing higher olefins by preferential reaction of the higher olefins with a benzene compound. In the presence of 0.001-0.03 mole of aluminum chloride per mole of benzene at not more than 50° in a closed vessel at 10-50 lb/sq in, the higher olefins, *e.g.*, propene, butenes, and pentenes, are removed from the gas mixture as liquid alkylbenzenes.[29]

When benzene containing sulfur impurities is treated with an olefin and aluminum chloride, alkylbenzenes are secured which are free from sulfur.[30]

The use of olefins as alkylating agents has been of commercial interest. Arylalkyl hydrocarbons secured by treatment of benzene with olefins in presence of aluminum chloride have been claimed as additives to motor fuels,[31] and as materials for preparation of synthetic detergents and wetting agents.[32] The manufacture of compounds useful in preparing

[29] U. S. P. 2,078,238 (1937) to R. R. Driesbach (to Dow Chemical Co.), *C. A.*, 31, 4346 (1937). Brit. P. 474,414 (1936) to Dow Chemical Co.; *Brit. Chem. Abs.*-B, 37 (1938).

[30] U. S. P. 1,953,702 (1934) to J. G. Davidson (to Carbide and Carbon Chem. Corp.); *Brit. Chem Abs.*-B, 140 (1935).

[31] U. S. P. 2,009,108 (1935) to G. Egloff (to Universal Oil Products), *Brit. Chem. Abs.*-B, 778 (1936); U. S. P. 1,994,249 (1935) to V. Ipatieff and A. V. Grosse (to Universal Oil Products), *C. A.*, 29, 2974; U. S. P. 2,010,948 (1935) to G. Egloff (to Universal Oil Products), *C. A.*, 29, 6606; Brit. P. 403,505 (1933) to Carbide and Carbon Chemicals Corp., *C. A.*, 28, 4568; U. S. P. 1,879,118 (1932) to J. D. Davidson (to Carbide and Carbon Chemicals Corp.), *C. A.*, 27, 401.

[32] U. S. P. 1,995,827 (1935) to C. A. Thomas (Sharples Solvents Corp.), *C. A.*, 29, 3349; U. S P. 1,992,160 (1935) to C. A. Thomas (to Sharples Solvents Corp.); Brit. P. 416,279 (1934) to I. G., *C. A.*, 29, 1906.

artificial musks has been described. It is claimed that *tert*-butyl-*m*-xylene is produced in almost theoretical amounts by passing isobutene through a mixture of *m*-xylene to which some isobutyl chloride or hydrogen chloride has been added.[33] Methyldiethylethylene with *m*-xylene in the presence of aluminum chloride readily yields 5-α,α-diethylpropyl-*m*-xylene (b.p. 257-259°/745 mm), which is useful in the formulation of perfumes.[34] Butylation of *m*-xylene, with production of *sym*-butylxylene may be effected by treatment with diisobutylene in the presence of aluminum chloride. Analogous reaction with toluene instead of *m*-xylene yields *m*- and *p*-butyltoluenes. The use of hydrogen chloride is advantageous in both reactions.[35]

Products useful as organic solvents and as dielectric agents are secured by reacting benzene, or a halobenzene containing not more than 3 halogen atoms, successively with ethylene and propylene in the presence of aluminum chloride. In most instances the products are liquid mixtures of isomeric ethyldiisopropylbenzenes.[36] Materials useful as dielectric agents, insecticides, and fumigants are secured by similarly alkylating aromatic hydrocarbons of the benzene series, having not more than 4 chlorine atoms attached to the benzene nucleus, with a complex mixture of gaseous olefins obtainable by cracking a petroleum fraction.[37]

The alkylation of naphthalene and also of other polynuclear hydrocarbons by reaction with olefins in the presence of aluminum chloride is well covered in the patent literature. However, according to Fischer and Schneider[38] naphthalene does not react with ethylene at 100-200° in presence of aluminum chloride. Reaction of polynuclear hydrocarbons with ethylene is more difficult than it is with higher olefins. Addition with ethylene may be effected at temperatures over 100° and under pressure. Under milder conditions, higher olefins are easily absorbed from a mixture of ethylene and higher olefins, whereas ethylene is not converted. The process can thus be applied to separation of ethylene from other olefins. Patents on reactions of olefins with polynuclear hydrocarbons in the presence of aluminum chloride are summarized in Table 22.

In their study of ethylation of hydrocarbons with olefins, Berry and Reid[18] and Milligan and Reid[17] prepared propyl- and ethylnaphthalenes by reacting naphthalene with the correspondingly alkylated benzenes in the presence of aluminum chloride. A transfer of alkyl groups was effected.

Cycloölefins and Aromatic Hydrocarbons

The addition of benzene to cyclohexene takes place vigorously in presence of aluminum chloride with formation of cyclohexylbenzene and

[33] German P. 184,230 to Aktien-Gesells. für Anilin-Fabrik., *J. Chem. Soc. Abs.*, 92 (I), 907 (1907).
[34] M. Battegay and M. Kappeler, *Bull. soc. chim. (4)*, 35, 989-996 (1924); *J. Chem. Soc. Abs.*, 126 (I), 1177 (1924).
[35] E. Noelting, *Chim. et. Ind.*, 6, 719-735 (1921); *C. Z.*, 1922, II, 750.
[36] U. S. P. 2,140,762 (1939) to R. R. Dreisbach (to Dow Chemical Co.); see also U. S. P. 2,193,760 (1940) to R. R. Dreisbach, E. C. Britton, and R. P. Perkins (to the Dow Chemical Co.) for alkylation of halobenzenes as a step in making *m*-alkylphenols.
[37] U. S. P. 2,174,069 (1939) to R. R. Dreisbach (to Dow Chemical Co.).
[38] F. Fischer and W. Schneider, Ges. Abhandlung Kennt. Kohle, 1, 227-230 (1917); *C. A.*, 13, 3189.

Table 22

Hydrocarbon	Olefin	Conditions	Product	Ref.
Tetralin	ethylene	50-100° at 20-30 atm	ethylated tetralin	7
Naphthalene or Tetralin	ethylene	100-200° at 20 atm	ethylated naphthalenes	6
Tetralin or Naphthalene	olefins	100-200°	alkyl naphthalene or tetralin	1
Naphthalene or deriv.	propylene or higher homologs	below 100° and not much above atm pressure	alkyl naphthalenes	4, 17
Naphthalene or Tetralin	olefinic gases	50-200°	alkyl naphthalenes	5
Naphthalene or Tetralin	ethylene or ethylene-contg. gases	100-200°; pressure	oily products	8
Naphthalene	propylene	.....	tetraisopropyl naphthalene	9
Naphthalene or Tetralin	propylene or higher olefins	.....	alkylated naphthalenes or tetralins	10
Naphthalene	higher olefins	elevated temp	fluorescent substances	12 14-15
Naphthalene	polymeric olefins	.....	material for detergents	18
Acenaphthene	propylene	.....	material for wetting agents	3
5-Bromoacenaphthene	propylene	.....	material for wetting agents	3
Acenaphthene	propylene	100-150° at 10-20 atm	lubes and resins	2
Anthracene	propylene	100-150° at 10-20 atm	lubes and resins	2
Anthracene	propylene	..	material for wetting agents	3
Anthracene	3-hexene	.. ...	x,x-di(1'-ethylbutyl)-anthracene	21
Anthracene	higher olefins	elevated temp.	fluorescent substances	12, 14, 15
Polynuclear hydrocarbons	higher olefins	70-250°; $AlCl_3$ + NaCl or $CuCl_2$	fluorescent substances	19
Anthracene	petroleum distillates	. ...	fluorescent substances	20
Phenanthrene	propylene	100-150° at 10-20 atm	resins and lubes	2
Phenanthrene	propylene	.....	material for wetting agents	3
Phenanthrene	higher olefins	elevated temp.	fluorescent substances	12, 14, 15
Biphenyl	propylene	90-95°	isopropylbiphenyls	11

Table 22—*(Continued)*

Hydrocarbon	Olefin	Conditions	Product	Ref.
Biphenyl, hydrogenated biphenyl, and chloro- or bromobiphenyl	olefins of less than 6 C atoms	75-90°	alkyl derivatives of corresponding biphenyls	16
Chlorohydroxybiphenyls	olefins	75-175°	alkylchlorohydroxybiphenyls	13

References

1. Brit. P. 265,601 (1927) to I. G.; Brit. P. 273,665 (1927) to I. G., *Brit. Chem. Abs.*-B, 740 (1928).
2. U. S. P. 1,741,478 (1929) to R. Michel (to I. G.). *C. A.*, 24, 1123; Brit. P. 323,100 (1929) to R. Michel.
3. Brit. P. 326,500 (1928) to I. G., *Brit. Chem. Abs.*-B, 501 (1930); French P. 665,262 (1930) to I. G.
4. German P. 525,834 (1927) to R. Michel (to I. G.), *C. A.*, 25, 4282.
5. German P. 523,691 (1928) to R. Michel (to I. G.), *C. A.*, 24, 5766.
6. U. S. P. 1,741,472 (1929) to R. Michel (to I. G.). *C. A.*, 24, 1120.
7. U. S. P. 1,766,344 (1930) to R. Michel (to I. G.). *C. A.*, 24, 4051. German P. 505,403 (1930) to I. G.
8. U. S. P. 1,667,218 (1928) to R. Michel, *C. A.*, 22, 1950.
9. Brit. P. 316,951 (1929) to I. G., *C. Z.*, 1930, I, 3724.
10. Brit. P. 295,990 (1928) to I. G., *Brit. Chem. Abs.*-B, 276 (1930).
11. Brit. P. 497,284 (1939) to du Pont.
12. U. S. P. 2,071,521 (1937) to H. Hartmann and H. Rabe (to I. G.).
13. U. S. P. 2,002,724 (1937) to E. C. Britton, G. H. Coleman, and L. E. Mills (to Dow Chemical Co.).
14. French P. 762,002 (1934) to I. G., *C. A.*, 28, 4590.
15. Brit. P. 409,696 (1934) to I. G., *C. A.*, 28, 6295.
16. U. S. P. 2,172,391 (1939) to H. J. Kraus (to Monsanto Chemical Co.).
17. U. S. P. 1,767,302 (1930) to R. Michel (to I. G.).
18. U. S. P. 1,992,160 (1935) to C. A. Thomas (to Sharples Solvents Corp.).
19. U. S. P. 2,028,472 (1936) to H. Rabe (to I. G.), *C. A.*, 30, 1989; German P. 603,269 (1934) to H. Rabe (to I. G.), *C. A.*, 29, 596.
20. U. S. P. 1,988,733 (1935) to S. S. Shaffer and E. V. Fasce (to Standard Oil Development Co.), *Brit. Chem. Abs.*-B, 1015 (1937).
21. L. Spiegler and J. M. Tinker, *J. Am. Chem. Soc.*, 61, 1002-1004 (1939).

higher-boiling products.[39] According to Bodroux[40] reaction with toluene can be effected so as to give a 63 per cent yield of cyclohexyltoluene, b.p. 255-61°/758 mm. He also reports the following data on addition of other alkylated benzenes to cyclohexane in presence of aluminum chloride:

Alkylbenzene	Product: -benzene	% Yield
p-Xylene	2-cyclohexyl-1,4-dimethyl-	45
	dicyclohexyl-1,4-dimethyl-	small amt.
m-Xylene	5-cyclohexyl-1,3-dimethyl-	81
Mesitylene	2-cyclohexyl-1,3,5-trimethyl-	35
Cymene	cyclohexyl-1-isopropyl-4-methyl-	40
	dicyclohexyl-1-isopropyl-4-methyl-	small amt.

According to Corson and Ipatieff[41] the products of the addition of benzene to cyclohexene in the presence of aluminum chloride depend upon the amount of cyclohexene used in the reaction. Mono- (I), di- (II), tri- (III), and tetra (IV)-cyclohexylbenzenes are formed as shown below:

[39] T. M. Berry and E. E. Reid, *loc. cit.* S. S. Nametkin and E. S. Pokrovskaya, *J. Gen. Chem. (U. S. S. R.)*, 7, 962-972 (1937); *C. A.*, 31, 5332.
[40] D. Bodroux, *Compt. rend.*, 186, 1005-1006 (1928); *C. A.*, 22, 2370.
[41] B. B. Corson and V. N. Ipatieff, *J. Am. Chem. Soc.*, 59, 645-647 (1937); *C. A.*, 31, 3585 (1937).

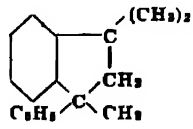
Benzene (g)	Cyclohexene (g)	$AlCl_3$ (g)	Products obtained, (g)
176	246	60	56—I 31—II 158—III 1—IV
156	328 and 150 g cyclohexane	60	20—I 35—II 150—III 80—IV

These investigators, as well as Nametkin and Pokrovskaja [41] found that a transfer of cyclohexyl groups from cyclohexylbenzenes to benzene occurs upon heating in the presence of aluminum chloride.

The production of cyclohexyl aromatic hydrocarbons or their halogen derivatives by reaction of cyclohexene with aromatic hydrocarbons or halogenated aromatic hydrocarbons in the presence of aluminum chloride is covered by a patent to Dow Chemical Company [42] An example cites the preparation of a monocyclohexylchlorobenzene by reaction of cyclohexene with chlorobenzene in presence of about 0.05 mole of aluminum chloride.

The reaction of cyclopentene with benzene and aluminum chloride has been investigated by Nametkin and Pokrovskaja.[43] Cyclopentylbenzene is the main reaction product. Some di- and tricyclopentylbenzenes were also found, the yield of the higher homologs depending on the ratio of cyclopentene to benzene used. Cyclopentylbenzene with cyclopentene yields di- and tricyclopentylbenzenes. Tetracyclopentylbenzene was obtained by reacting cyclopentene with dicyclopentylbenzene.

The addition of benzene to 2,4-diphenyl-4-methylpentene-2 has been reported [44] to result in production of a 20 per cent yield of the saturated dimer of α-methylstyrene, 1,1,3-trimethyl-3-phenylhydrindene:



Naphthalene or tetralin reacts with cyclopentene [45] or cyclohexene [46] to give a mixture of mono- and polycyclopentyl or cyclohexylnaphthalenes or tetralins.

Reaction of Olefins with Phenols

The addition of olefins to phenols in the presence of aluminum chloride constitutes a commercial method for the preparation of nuclear

[41] U. S. P. 1,969,984 (1934) to Dow Chemical Co.; *C. A.*, **28**, 6156.
[42] S. S. Nametkin and E. S. Pokrovskaja, *J. Gen. Chem. (U. S. S. R.)*, **8**, 695-718 (1938)
[43] E. Bergmann, H. Taubadel, and H. Weiss, *Ber.*, **64**, 1493-1501 (1931).
[44] E. S. Pokrovskaja and R. J. Suschtschik, *J. Gen. Chem (U. S. S. R.)*, **9**, 2291-2301 (1939), *Brit. Chem. Abs.-A*, II, 160 (1940).
[45] E. S. Pokrovskaja and T. G. Stepantzeva, *J. Gen. Chem (U. S. S. R.)*, **9**, 1953-1960 (1939), *Brit. Chem. Abs.-A*, II, 161 (1940).

alkylated phenols. The reaction appears to be a general one, but as in other additions of this type, it is most readily effected with olefins of at least 3 carbon atoms. Phenol, substituted phenols, or naphthols have been specified as phenolic constituents. The use of a small amount of alkyl chloride or of hydrogen halide is advantageous in initiating the reaction. Solvents, for example, carbon tetrachloride, may be used.[47] The alkylated phenols, especially *p-tert*-butylphenol, are used in preparation of oil-soluble phenol-aldehyde resins.

A 77.8 per cent yield of *p-tert*-butylphenol has been secured by reacting 56 g of isobutylene, 94 g of phenol, 9 g of *tert*-butyl chloride, and 5 g of aluminum chloride at 100° and 5 atmospheres' pressure for two minutes.[48]

Diisobutylene may be used as the olefin for preparation of *p-tert*-butylphenol. Such a process consists in reacting phenol with a polyisobutylene at 110-190° in the presence of a Friedel-Crafts catalyst.[49] According to Smith and Rodden,[50] the product of the reaction of diisobutylene with phenol and aluminum chloride depends upon reaction conditions. When 1½ moles of aluminum chloride are gradually added to a mole of phenol, a half mole of diisobutylene is slowly added with heating, and the reaction mixture is subsequently heated on a steam-bath for six hours, the products consists of *tert*-butylphenol in 67 per cent yield and 4-(1,1,3,3)-(tetramethylbutyl)phenol in 14 per cent yield. More vigorous conditions favor the formation of only *tert*-butylphenol, whereas much milder conditions tend to produce the (tetramethylbutyl)phenol almost completely.

The condensation of phenols with cracked gasolines containing substantial quantities of olefins in the presence of aluminum chloride leads to production of alkylated phenols which may be used in the manufacture of aldehyde resins.[51]

Ring closure takes place in the condensation of di-tertiary 1,5-diolefins with phenols and aluminum chloride. 2,5-Dimethyl-1,5-hexadiene and phenol thus yield 5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-2-naphthol, together with a lesser amount of a chromane derivative, formed by reaction of the first product with an additional mole of the diolefin.[52] This reaction, involving cycli-alkylation through addition at both double bonds, is noteworthy because, in general, diolefins are readily polymerized in the presence of aluminum chloride.

Reaction of Olefins with Phenol Ethers

The alkylation of phenol ethers may be effected by reaction with olefins in presence of aluminum chloride. According to Seide and

[47] U. S. P. 1,892,900 (1933) to F. Lunner (to Beck, Koller, & Co.); *C. A.*, **27**, 2319; French P. 697,711 (1930) to Soc Reichhold, Flugger, and Boecking, *C. A.*, **25**, 3013; Austrian P. 124,281 (1931) to F. Lunner (to Soc. Reichhold, Flugger, and Boecking), *C. A.*, **26**, 735.

[48] V. I. Isagulyants and P. P. Bagryantseva, *Neftyanoe Khoz.* (1938), No. 2, 36-41; *C. A.*, **33**, 8183.

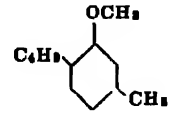
[49] U. S. P. 2,091,565 to R. P. Perkins and H. S. Nutting (to Dow Chemical Co.).

[50] R. A. Smith and C. J. Rodden, *J. Am. Chem. Soc.*, **59**, 2353 (1937).

[51] Fr. P. 805,913 (1936) to Soc. francaise Beckacite, *C. A.*, **31**, 4343 (1937); Brit. P. 473,438 (1937) to Beck, Koller & Co.; U. S. P. 2,154,192 (1939) to A. Zinke (to Beck, Koller & Co.).

[52] H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, **62**, 38-44 (1940).

Dubinin,[53] the reaction of isobutene with *m*-cresol methyl ether and aluminum chloride yields only *o*-butyl-*m*-cresol methyl ether, m.p. 23-24°,



Alkylation effected by passage of isobutene into 5 per cent solutions of aluminum chloride in a phenol ether gave the following results[54]:

Phenol ether	Product	% Yield
o-Cresol methyl ether	*tert*-butyl-*o*-cresol methyl ether, b.p.$_{21}$ 112-3°	58
p-Cresol methyl ether	3-*tert*-butyl-*p*-cresol methyl ether, b.p.$_{21}$ 94-95°	61
Resorcinol dimethyl ether	4-*tert*-butylresorcinol dimethyl ether, b.p.$_{21}$ 120-2°	71

The production of the methyl ether of *tert*-butyl-*m*-cresol by reaction of *m*-cresol methyl ether for about a half hour in the presence of aluminum chloride has been patented.[55] Another patent claims alkylation of cresol methyl ethers by passage of isobutene or propene into a mixture of 366 g of the ether and 36 g of aluminum chloride at 0° until a 100-g increase in weight has occurred. The following products are claimed[56].

Ether	Olefin	Product
m-Cresol methyl ether	isobutene	1-methyl-3-methoxy-4-*tert*-butylbenzene b.p. 228°
m-Cresol methyl ether	propene	a mixture of methyl ethers of isomeric thymols, b.p. 215-230°
p-Cresol methyl ether	isobutene	1-methyl-4-methoxy-3-*tert*-butylbenzene b.p. 226°
o-Cresol methyl ether	isobutene	1-methyl-2-methoxy-*tert*-butylbenzene, b.p. 232°

The reaction of di-tertiary 1,5-diolefins with phenols resulting in the formation of higher ring compounds * is also applicable to phenol ethers

Addition of Aromatic Compounds to Unsaturated Carboxylic Acids

As with olefinic hydrocarbons, addition of aryl groups at the double bond may be effected by reaction of unsaturated carboxylic acids with aromatic compounds in presence of aluminum chloride. With the exception of those effected with oleic acid, reports of such reactions with other acids are sketchy and often contradictory. A great deal of the confusion concerning the identity of reaction products is undoubtedly

[53] O. A. Seide and B. M. Dubinin, *J. Gen. Chem. (U. S. S. R.)*, 2 (64), 455-471 (1932), *C. A.*, 1933, I, 604.
[54] B. M. Dubinin, *Compt. rend. acad. Sci. U. R. S. S.*, 3, 263-266 (1935); *C. A.*, 30, 1870, *C. A.*, 1936, I, 4561.
[55] U. S. P. 1,927,053 (1933) to E. Wonderwahl (to Givaudan-Delawanna, Inc.); *C. A.*, 27, 5752.
[56] French P. 725,577 (1932) to Schering-Kahlbaum, *C. Z.*, 1932, II, 932-933; Brit. P. 373,896 (1931) to Schering-Kahlbaum, *Brit. Chem. Abs.*-B, 573 (1932).

* See page 467.

due to the fact that the aryl-substituted acids secured are generally oils. Little is known about the orientation of the entering aryl group. In the case of the reaction with oleic acid, it has been pointed out [57] that the product is an approximately equal mixture of 9- and 10-phenyloctadecanoic acid, addition thus occurring at either of the unsaturated carbons. The wide boiling ranges of products of similar reaction indicate general formation of isomeric products. Although several investigators [58] have stated that yields of arylated acids increase with the distance between the double bond and the carboxy- group of the unsaturated acid, experimental evidence is too meager to substantiate this generality. Reactions with unsaturated aliphatic acids, from acrylic to oleic, have been reported, and analogous reactions have been found to take place with unsaturated dicarboxylic acid, aralkyl acids, and alicyclic acids. Yields, thorough characterization of products, and reaction conditions are not often given. Since aluminum chloride has a polymerizing effect on unsaturated acids, by-products of the reaction are frequently resinous materials. Aluminum chloride has been shown to have not only a polymerizing effect [59] on oleic acid, but also a decomposing action.[60]

In 1908, Eijkman [61] reported that when unsaturated aliphatic or aralkyl acids are reacted with benzene in the presence of aluminum chloride, addition of the phenyl residue occurs at the double bond, with production of aryl-substituted saturated acids. Crotonic acid thus yields β-phenylbutyric acid

$$CH_3.CH:CH.COOH + C_6H_6 \xrightarrow{AlCl_3} CH_3.CH(C_6H_5).CH_2COOH$$

The following series of condensations, most of which were effected by maintaining a mixture of the unsaturated acid with the hydrocarbon and aluminum chloride at 30° for four weeks, are reported by Eijkman:

Hydrocarbon	Acid	Product
Benzene	crotonic	β-phenylbutyric acid
Toluene	crotonic	no addition product
Benzene	Δ^1-isopentenic acid $(CH_3)_2C:CH.COOH$	phenylisopropylacetic acid $(CH_3)_2CH.CH(C_6H_5).COOH$
Toluene	Δ^1-isopentenic acid	tolylisopentanic acid
Benzene	tiglic acid $CH_3CH:C(CH_3).COOH$	α,β-dimethyl-β-phenylpropionic acid $CH_3.CH(C_6H_5).CH(CH_3).COOH$
Benzene	cinnamic $C_6H_5.CH:CHCOOH$	β,β-diphenylpropionic acid $(C_6H_5)_2CH.CH_2.COOH$
Benzene	α-methylcinnamic $C_6H_5.CH:C(CH_3).COOH$	α-methyl-β,β-diphenylpropionic acid $(C_6H_5)_2CH.CH(CH_3).COOH$
Benzene	α-ethylcinnamic	α-ethyl-β,β-diphenylpropionic acid
Benzene	α-phenylcinnamic	α,β,β-triphenylpropionic acid

[57] J. Harmon and C. S. Marvel, *J. Am. Chem. Soc.*, 54, 2515-2527 (1932).
[58] E. Fourneau and P. M. Baranger, *Bull. soc. chim.* (4), 49, 1161-1173 (1931); *Brit. Chem. Abs.*-A, 1290 (1931); *C. Z.*, 1931, II, 3467-8. J. Marcusson, *Z. angew. Chemie*, 33, 231-232, 234-235, 237-241 (1920); *C. A.*, 15, 818; *C. Z.*, 1920, IV, 687-688.
[59] J. Marcusson, *loc. cit.*
[60] N. D. Zelinsky and K. P. Lawrowsky, *Ber.*, 61, 1054-1057 (1928)
[61] J. F. Eijkman, *Chem. Weekblad*, 5, 653-666 (1908); *C. Z.*, 1908, II, 1100; *J. Chem. Soc. Abs.*, 94 (I), 794 (1908).

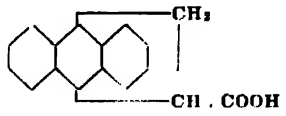
Previously, Eijkman [62] had also reported the following reactions with benzene:

Acid	Product
Phenylisocrotonic	γ,γ-diphenylbutyric acid
Allylacetic	γ-phenylvaleric acid
β,γ-Hydrosorbinic ($CH_3.CH_2.CH:CH.CH_2.COOH$)	phenylhexyl acid
β,γ-Hydropiperinic ($CH_2O_2.C_6H_3.CH_2CH:CHCH_2.COOH$)	no satisfactory results
Allylmalonic	no aromatic substituted acid; gives lactones instead
Isolauronolic	phenyldihydroisolauronolic acid
β-Campholenic	phenyldihydrocampholenic acid (slow reaction)

Reaction of acrylic acid with benzene in the presence of aluminum chloride has been claimed to yield β-phenylpropionic acid [63]:

$$CH_2:CHCOOH + C_6H_6 \xrightarrow{AlCl_3} C_6H_5.CH_2.CH_2.COOH$$

The condensation of acrylic acid with anthracene in the presence of aluminum chloride has been claimed to give an addition compound (m.p. 187-188°) having the following structure,



and an analogous compound (m.p. 232°) from cinnamic acid. Similar products are secured from acrylic acid and *ms*-dichloroanthracene, 1,5-dichloroanthracene, 2,7-dimethylanthracene, α-anthrol, or phenanthrene. When anthracene is reacted with maleic acid, a β-lactone is formed.[64]

Dimethylacrylic acid has ben reacted with alkylbenzenes to give normal double-bond addition products. Thus, 5 g of dimethylacrylic acid with *p*-xylene and aluminum chloride at 0° gives 4.12 g of β-(2,5-dimethylphenyl)isovaleric acid. Mesitylene, hemimellitene, and pseudocumene react analogously, although rearrangement of alkyl groups occurs with the latter. The product from mesitylene was a dimethylphenylisovaleric acid.[65] Obviously during the condensation of dimethylacrylic acid with trialkyl benzenes, the alkyl groups are split off or rearranged.

It has been recently noted by Nenitzescu and his co-workers [66] that in the reaction of aliphatic α-β-unsaturated acids with benzene in the presence of aluminum chloride, the phenyl group does not take the position

[62] J. F. Eijkman, *Chem. Weekblad*, 4, 727-738 (1907); *C. Z.*, 1907, II, 2048.
[63] German P. 666,468 (1938) to H. Hopff (to I. G.); *C. A.*, 33, 2149.
[64] Brit. P. 308,339 (1927) to I. G.; *Brit. Chem. Abs.*-B, 237 (1929).
[65] L. I. Smith and W. W. Prichard, *J. Am. Chem. Soc.*, 62, 771-7 (1940).
[66] C. D. Nenitzescu, I. G. Gavat and D. Cocora, *Ber.*, 73, 233-7 (1940).

which had been occupied by the double bond. Thus, 2-hexenoic acid gives 5-phenylcaproic acid and 3-methyl-2-hexenoic acid gives exclusively 3-methyl-5-phenylcaproic acid. With the assumption that these reactions proceeded through intermediate formation of saturated aliphatic chloro-acids, an attempt to isolate the chloro-acid from 2-hexenoic acid was unsuccessful, although some chlorine was detected in the product resulting from the treatment of the acid with aluminum chloride and carbon disulfide. It was found, however, that 2-hexenoic acid was converted to the 3- or 4-isomer during the treatment. It was thus concluded that a successive addition and elimination of hydrogen chloride had occurred and that the production of, *e.g.*, 5-phenylcaproic acid from 2-hexenoic acid was due, not to halogen migration in the intermediately formed chloro-acid, but to this elimination and reintroduction of hydrogen halide; this also explains why the phenyl group does not go to the end carbon.

The condensation of olefinic acids with benzene in the presence of aluminum chloride has been studied with the object of obtaining products of therapeutic value.[67] Undecylenic acid with benzene gave two acids, which were considered to be ω or ω'-phenylundecyl acids, whose amides melted at 57° and 79°, respectively. Undecylenic acid was also found to condense with benzylcyanide with formation of phenylacetonitrile-4-undecoic acid, $NC.CH_2.C_6H_4.(CH_2)_{10}.COOH$. From a long study of similar reactions, it was found that the esters of the olefinic acids afford higher yields than the free acids, and that the yields increase with the distance between the double linking and the carboxyl group.

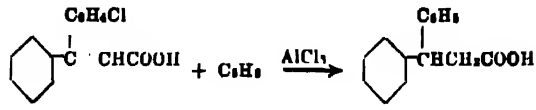
Using the method of Eijkman[62] and of Czensny[68] Wislicenus and Eble[69] prepared β,β-diphenylpropionic acid from cinnamic acid and benzene. To a solution of 30 g of the acid in about 300-350 g of benzene, 50 g of powdered aluminum chloride was slowly added. If the temperature was constantly kept at below 10°, the yield was almost quantitative. These investigators prepared the ethyl ester of the diaryl acid and reported for it a melting point of 22-23°.

It has been found that reaction of *o*- or *p*-chlorocinnamic acid with benzene and aluminum chloride results in formation of one product, β,β-diphenylpropionic acid.[70] In analogous reaction of *o*- or *p*-chlorocinnamic acid with chlorobenzene, the addition products were also identical, β,β-bis(*p*-chlorophenyl)-propionic acid being secured. The anomalous course of these reactions has been explained by assuming a reversible reaction. In each case the normal addition products were formed, elimination of a chlorophenyl group occurred, and subsequent reaction of the halogen-free acid with benzene or chlorobenzene gave β,β-diphenylpropionic acid or β,β-bis(*p*-chlorophenyl)propionic acid respectively.

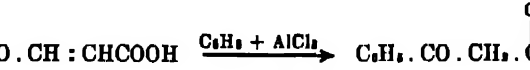
Hydrogenation, as well as replacement of an aryl group, has been

[67] E. Fourneau and P. M. Baranger, *Bull. soc. chim.* (4), 49, 1161-1172 (1931); *Brit. Chem. Abs.*-A, 1290 (1931); *C. Z.*, 1931, II, 3467-3468.
[68] Czensny, Diss., Halle, 1912, p. 19.
[69] W. Wislicenus and K. Eble, *Ber.*, 50, 256-262 (1917).
[70] R. C. Fuson, A. P. Kozacik, and J. T. Eaton, *J. Am. Chem. Soc.*, 55, 3799-3803 (1933).

observed in the reaction of β-(*p*-chlorophenyl)cinnamic acid with benzene and aluminum chloride [71]:



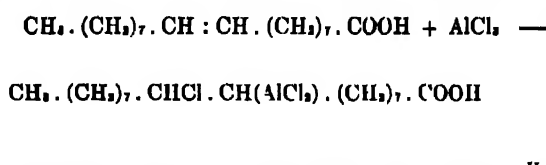
Unsaturated keto- acids have been shown to add benzene or toluene at the double bond.[72] β-Benzoylacrylic acid, prepared by reaction of maleic anhydride with benzene in presence of aluminum chloride, reacts according to the scheme:



A large excess of the catalyst and benzene is necessary for the reaction and the yield of α-phenyl-β-benzoylpropionic acid is low. An analogous addition takes place with toluene, with production of α-tolyl-β-benzoylpropionic acid. β-Toluylacrylic acid with toluene similarly gives a 20 per cent yield of α-tolyl-β-toluylpropionic acid.

Reaction with Higher Unsaturated Fatty Acids

According to Marcusson,[73] the reaction of oleic acid with benzene in the presence of aluminum chloride proceeds according to the scheme.



Elaidic acid was found to react analogously. The reaction appeared to be of general applicability with homologs of benzene, naphthalene, anthracene, nitrobenzene, anisole, phenetole, etc. The condensation products were thick liquids. The product from oleic acid and anthracene was distinguished by its high viscosity. Acids in which the olefinic bond was adjacent to the carboxyl group, for example, *n*-crotonic acid or phenylacrylic acid, did not undergo the reaction. This contradicts the earlier work of Eijkman.[62] Unsaturated acids, that is, those which absorbed no methyl iodide from the Hübl solution, did not add aluminum chloride, and, therefore, did not condense with benzene. The fact that phenylation did not occur if the double bond were in the α-position to the car-

[71] L. L. Alexander, A. L. Jacoby, and R. C. Fuson, *J. Am. Chem. Soc.*, **57**, 2368-2369 (1935).
[72] R. Pummerer and E. Buchta, *Ber.*, **69**, 1005-1017 (1936).
[73] J. Marcusson, *Z. angew. Chem.*, **33**, 221-222, 234-235 (1920); *C. Z.*, 1920, IV, 687-688.

boxyl group is of interest in that Poncio and Gastaldi [74] had previously pointed out that the further removed is the double bond from the carboxyl group, the more closely does the experimental iodine number approach the theoretical iodine number of unsaturated acids.

A 35 per cent yield of phenylstearic acid was secured by Nicolet and de Milt [75] who added 100 g (1.2 molecular proportions) of aluminum chloride to 200 cc of oleic acid dissolved in 400 g of dry benzene, and after the violent reaction had moderated, gradually heated the reaction mixture to 80°, and kept it at this temperature for about six hours, or until evolution of hydrogen chloride had ceased. The position of the phenyl group was not proved, but the product was considered to be probably 10-phenylstearic acid. The material upon which the yield was based had a boiling range of about 230-250°/4 mm.

From a study of the effect of varying the amount of aluminum chloride in the reaction of oleic acid with benzene, Schmidt [76] has concluded that production of phenylstearic acid proceeds with great speed in the presence of approximately equimolecular quantities of aluminum chloride and oleic acid and an excess of benzene. Reaction was found to be practically complete in less than five minutes. If a considerable excess of aluminum chloride is used, or prolonged boiling of the reaction mixture is effected, products are formed which have lower neutralization equivalents than that of phenylstearic acid. With less than one-third of the equivalent quantity of aluminum chloride, very little condensation occurs.

Reaction of oleic acid with xylene was found to proceed with equal rapidity.

According to Harmon and Marvel,[77] the phenyloctadecanoic acid prepared by Nicolet and de Milt [75] and by Schmidt [76] is a mixture of about equal parts of 9- and 10-phenyloctadecanoic acids. When these acids were prepared by the malonic ester synthesis, they had the following constants:

	b.p °C	b.p mm	n_D^{20}	sp gr $\frac{25}{25}$
9-phenyloctadecanoic acid	200-204	.09	1.4891	0.9340
10-phenyloctadecanoic acid	199-205	.09	1.4894	0.9338

Preparation of phenyloctadecanoic acid according to the method of Nicolet and de Milt gives a product having the following constants:

b.p. °C	b.p. mm	n_D^{20}	sp gr $\frac{25}{25}$
199-203	.08	1.4906	0.9377

p-Bromophenacyl esters were prepared of the three products. The purified esters had the following melting points:

[74] G. Poncio and C. Gastaldi, *Gazz. chim. ital.*, 42 (II), 92-95; *C. Z.*, 1912, II, 1154.
[75] B. H. Nicolet and C. M. de Milt, *J. Am. Chem. Soc.*, 49, 1103-1106 (1927).
[76] E. G. Schmidt, *J. Am. Chem. Soc.*, 52, 1172-1174 (1930).
[77] J. Harmon and C. S. Marvel, *J. Am. Chem. Soc.*, 54, 2515-2527 (1932).

	m.p. (°C)	No. of crystallizations
9-isomer	83.5-84.5	7
10-isomer	71-72	6
Product from oleic acid and benzene	79-82	14

Indications are that the product prepared according to the procedure of Nicolet and de Milt is an approximately equal mixture of 9- and 10-phenyloctadecanoic acids.

An improved method of producing phenylstearic acid from oleic acid and benzene in presence of aluminum chloride has been claimed.[77a] Anhydrous oleic acid (350 parts) is dissolved in 600-900 parts of anhydrous benzene, the solution is heated to about 78-80°, and is gradually added to 180-200 parts of aluminum chloride which has been wetted with anhydrous benzene.

Kimura and his co-workers [78] report that phenylstearic acid is advantageously prepared by adding, with stirring, during five minutes, 56 g of aluminum chloride to a solution of 80 g of oleic acid in 450 cc of thiophene-free benzene, and subsequently heating the reaction mixture on a water-bath for two to three hours. Upon cooling, the reddish-brown reaction mixture was diluted with 1200 cc of ether, and then slowly treated, with stirring, with 800 cc of 20 per cent hydrochloric acid. The ethereal solution was washed neutral with water, dried with anhydrous sodium sulfate, and distilled *in vacuo*. There was secured 95 g of a dark red oil. This crude phenylstearic acid was fractionated at 4 mm in a stream of carbon dioxide; the fraction boiling at 260-270° was collected. Purification was effected by treatment of 400 g of the fraction, dissolved in 500 cc of ether, with about 5 g of activated carbon, heating with reflux on a water-bath for 30 minutes, and allowing the whole to stand overnight. Distillation of the filtered solution gave a purified phenylstearic acid having an acid number of 162.

For the identification of phenylstearic acid, prepared by phenylation of oleic acid, Kimura and Taniguti [79] prepared the following crystalline derivatives:

S-benzylthiuronium salt, m.p. 143-145°
p-xenylamide, m.p. 91-92°
p-iodophenacyl ester, m.p. 34-35°
p-phenylphenacyl ester, m.p. 35-40° (crude product)
benzimidazole derivative is an orange-yellow oil

According to Stirton and Peterson,[80] arylstearic acids from oleic acid are best prepared if an excess of the aromatic component is used, a 7:1 ratio of the aromatic compound to oleic acid being desirable. These investigators report the following condensations with oleic acid. The yields given represent a fraction after 2 vacuum distillations.

[77a] U. S. P. 1,972,566 (1934) to R. H. McKee and H. B. Faber; *C. A.*, 28, 6446.
[78] W. Kimura, T. Omura, and H. Taniguchi, *Ber.*, 71, 2686-2687 (1938).
[79] W. Kimura and H. Taniguti, *J. Soc. Chem. Ind. Japan* 42, Suppl. binding, 234-235 (1939); *C. A.*, 33, 8501.
[80] A. J. Stirton and R. F. Peterson, *Ind. Eng. Chem.*, 31, 556-558 (1939).

Aromatic component	Product: -stearic acid	% of Theoretical Yield
Benzene	phenyl-	38
Toluene	tolyl-	38
Xylene	xylyl-	47
Chlorobenzene	chlorophenyl-	25
Bromobenzene	bromophenyl-	22
Diphenyl ether	phenoxyphenyl-	29
Anisole	methoxyphenyl-	35

Reaction was effected by adding in portions at room temperature during fifteen minutes 100 g (0.75 mole) of aluminum chloride to a solution of 200 g (0.709 mole) of oleic acid in an excess of the aromatic compound, raising the temperature slowly to 80°, and maintaining it at this temperature for six hours. The reaction mixture was agitated continuously. It was found that yields were not increased by adding a solution of oleic acid to a suspension of aluminum chloride in the aromatic compound.

The arylstearic acids have been suggested for use as addition agents to lubricants,[81] and the soaps of phenylstearic acid have been investigated as materials for the preparation of lubricating greases.[82]

The reaction of oleic acid with naphthalene in the presence of aluminum chloride has been used for preparing a Twitchell reagent. A mixture of the acid and naphthalene is treated with 1.33 mole of Al_2Cl_6 and the reaction mixture is heated for one hour at 60°. The aluminum salt of 9 (or 10)-α-naphthylstearic acid was secured. Purification of the free acid was effected by long extraction with benzene. The free acid could not be crystallized.[83]

It has been found[84] that optimum conditions for the tolylation of camelia oil comprise the use of a 30 per cent excess of aluminum chloride, 1400 per cent excess toluene, and a temperature between 25 and 34°. Reaction is rapid and is usually complete in three hours. The product was a light-orange, clear, viscous oil, d_{30} 9429, n_{30} 1.4890, sapon. no. 158.31, esterification no. 152.3, and iodine no. 10.64. The mixture of tolylstearic acids obtained was purified through the methyl esters, from which a *p*-xenylamide (m.p. 86.5°) was isolated as the main product.[85]

Plastic materials have been claimed as products of the reaction of rubber, dissolved in an inert solvent, with unsaturated fatty acids of at least 6 carbon atoms in the presence of aluminum chloride.[86] Examples cite the use of oleic and linolenic acids.

Δ^1-Cyclohexenyl Acetic Acid

The identity of the product resulting from the addition of benzene to Δ^1-cyclohexenylacetic acid in the presence of aluminum chloride has been

[81] A. J. Stirton and R. F. Peterson, *loc. cit.*; U. S. P. 2,106,247 (1938) to A. H. Gleason; U. S. P. 1,850,561 (1932) and U. S. P. 2,043,536 (1936) to R. C. Moran; U. S. P. 2,081,075 (1937) and U. S. P. 2,095,528 (1937) to A. C. Vobach.

[82] W. S. Gulfoil, *Ind. Eng. Chem.*, 22, 487 (1930).

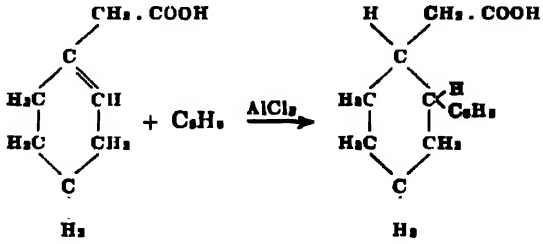
[83] K. Schlutius, *J. prakt. Chem.*, 142, 49-78 (1935); *C. A.*, 29, 4195.

[84] W. Kimura and J. Tsurugi, *J. Soc. Chem. Ind. Japan*, 42, Suppl. binding, 193-196 (1939) (in German); *C. A.*, 33, 8591.

[85] W. Kimura and J. Tsurugi, *J. Soc. Chem. Ind. Japan*, 42, 390-391 B (1939); *Brit. Chem. Abs.*, AII, 129 (1940).

[86] British P. 511,234 (1939) to Armour and Co.

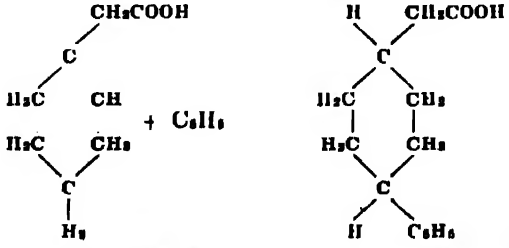
a matter of some study. The reaction would be expected to occur with production of 2-phenylcycloacetic acid,



and it has been reported [87] to proceed in this way. According to Cook,[88] however, the reaction is accompanied by migration of double bonds, and gives, not 2-phenylcycloacetic acid, but the 4-phenyl isomer. Subsequently Ghosh [89] repeated the reaction and stated that the product was 2-phenylcyclohexylacetic acid (m.p. 69-70°), and that the same compound was prepared also by condensation of hexahydro-α-coumaranone and benzene in the presence of aluminum chloride. He did not give the mixed melting point of the acids obtained from the two sources, since the individual products themselves did not have sharp melting points According to Cook, Hewett, and Lawrance,[90] the two stereoisomeric 2-phenylcyclohexylacetic acids have melting points of 84-85° and 168-170°.

In order to learn more about the reaction, Cook and Goulden [91] studied the addition of benzene to Δ^1-cyclohexenylacetic acid in presence of aluminum chloride at 0°, at room temperature, and on a boiling water-bath. In all cases they secured a moderately good yield of a liquid mixture of acids from which a 7 per cent yield of 4-phenylcyclohexylacetic acid (m.p. 112.5-113.5°) was secured. This product was converted into an amide, m.p. 195-196°. The amide of the acid secured by Ghosh was reported to melt at 196-197°. Cook and Goulden did not investigate the nature of the other acids secured, but they showed that 2-phenylcyclohexyl-acetic acids were not present, since these are dehydrated by treatment with sulfuric acid, whereas the liquid mixture of acids is sulfonated

Obviously migration occurs during the reaction:

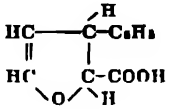


[87] R. Ghosh, *Science and Culture*, 1, 299 (1935), *Brit. Chem. Abs.*-A, 1495 (1935)
[88] J. W. Cook, *Chem. and Ind.*, 56, 290 (1937)
[89] R. Ghosh, *Science and Culture*, 3, 55-56 (1937); *C. A.*, 31, 7868.
[90] J. W. Cook, C. L. Hewett, and C. A. Lawrance, *J. Chem. Soc.*, 71-80 (1936)
[91] J. W. Cook and F. Goulden, *J. Chem. Soc.*, 1558-1560 (1937).

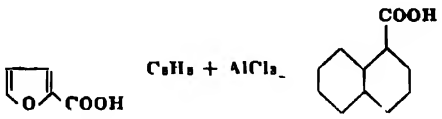
A migration of this type has likewise been observed by Nenitzescu and Curcăneanu [92] in the condensation of 1,2-dibromocyclohexane with benzene in the presence of aluminum chloride. In this case no 1,2-diphenylcyclohexane was formed, the products being 1,3- and 1,4-diphenylcyclohexanes.

Furoic Acid

The reaction of benzene with 2-furoic acid and aluminum chloride has been reported by King [93] to result in a product which was believed to be 3-phenyl-2,3-dihydro-2-furoic acid,



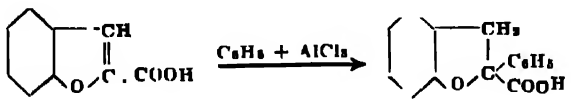
Addition was assumed to occur at the double bond. Gilman and his co-workers [94] have shown, however, that the product is really α-naphthoic acid, probably occurring as a consequence of 1,4-addition, and subsequent elimination of the oxygen bridge by intramolecular dehydration.



An analogous reaction takes place when chlorobenzene, toluene, or anisole is substituted for benzene, the corresponding 6-substituted-1-naphthoic acids being secured.[95]

Coumarilic Acid

The addition of benzene to coumarilic acid has been reported by King [93] to result in formation of α-phenyl-α,β-dihydrocoumarilic acid, m p. 68-69°:



Addition of Aromatic Compounds to Unsaturated Esters

It has been found that benzene or its derivatives adds more readily to the double bond of olefinic esters than it does to that of the free acid. With the object of obtaining esters of medicinal value in treating leprosy, esters of undecenoic and hydnocarpic acid have been condensed with ben-

[92] C. D. Nenitzescu and D. Curcăneanu, *Ber.*, 70, 346-348 (1937).
[93] E. J. King, *J. Am. Chem. Soc.*, 49, 563-566 (1927).
[94] H. Gilman, M. McCorkle, and N. O. Calloway, *J. Am. Chem. Soc.*, 56, 745 (1934); *C. A.*, 28, 2709.
[95] M. McCorkle and J. A. V. Turck, *Proc. Iowa Acad. Sci.*, 43, 205-206 (1936); *C. A.*, 32, 4101.

zene and some of its derivatives in the presence of aluminum chloride.[96] None of the substances prepared had any therapeutic value. It was found that yields increased with the distance between the olefinic bond and the carboxy- group, and that derivatives of benzene containing *para*-directing substituents gave better yields than benzene itself. The following reactions are described:

Expt	Benzene or derivative	Ester	$AlCl_3$	Products
1	40 moles benzene	1 mole undecylenic acid ethyl ester	1 mole	ω- and ω′-phenylundecanoic acid ethyl ester
2	40 moles benzene	1 mole hydnocarpic acid ethyl ester	1 mole	phenyldihydrohydnocarpic acid ethyl ester
3	96 g anisole (in 100 g petroleum ether)	53 g undecylenic acid ethyl ester	134 g	*p*-methoxyphenylundecanoic acid ethyl ester
4	96 g anisole (in 100 g petroleum ether)	53 g hydnocarpic acid ethyl ester	134 g	*p*-methoxyphenyldihydrohydnocarpic acid ethyl ester
5	55 g anisole (in 100 g petroleum ether)	20 g allylmalonic acid ethyl ester	85 g	*p*-methoxyphenylpropylmalonic acid ethyl ester
	40 g benzene	55 g undecylenic acid ethyl ester	40 g	phenylenediundecanoic acid diethyl ester
	136 g phenylacetic acid	106 g undecylenic acid ethyl ester	200 g (in 500 g CS_2)	ω-[4-(carboxymethyl)-phenyl]-α-carbethoxy decane
	136 g β-phenyl propionic acid	106 g undecylenic acid ethyl ester	200 g	phenyldimethylene-decamethylene-dicarboxylic acid-(1,4)-monoethyl ester. [COOH $CH_2.CH_2$ C_6H_4-$(CH_2)_{10}$ $CO_2C_2H_5$]
9	30 g benzyl cyanide	10 g undecenyl acetate	7 g	4-(ω-acetoxyundecyl)-phenylacetonitrile [NC CH_2 C_6H_4 $(CH_2)_{11}$-O CO.CH_3]

Reactions 1-4 were effected by introducing the catalyst to a mixture of the reactants at 35° and then allowing the mixture to stand until reaction had ended (by testing with bromine). Reaction 5 required twelve hours for completion. The formation of the dicarboxylic acid in reaction 6 was due to the proportion of the reactants used, as well as to the fact that the reaction mixture was heated for three hours. In reactions 7-8 the aralkyl acid was added to the catalyst in carbon disulfide under cooling, the unsaturated ester was added to this mixture, and the whole was heated to boiling for one hour. The reaction mixture of experiment 9 was heated for fifteen hours at 60°.

Condensation of oleyl acetate with benzene in presence of aluminum chloride has been used for the preparation of phenylstearic alcohol[97]

[96] E. Fourneau and P. M. Baranger, *Bull. soc. chim. (4)*, **49**, 1161-1173 (1931); *Brit. Chem. Abs.*-A, 1200 (1931); *C. Z.*, 1931, II, 3467-8.

[97] J. P. Sisley, *Chim. et ind.* Special No. 763-764 (April, 1934); *C. A.*, **28**, 5813; *Brit. Chem. Abs.*-A, 768 (1934).

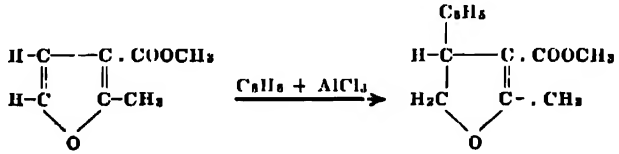
Phenylstearic acetate was prepared by gradually adding 80 g of oleyl acetate in benzene solution to 34.5 g of aluminum chloride moistened with benzene, gradually raising the temperature to 65°, and heating at this temperature for ten hours. A total of 200 g of benzene was used. Saponification of the phenylstearic acetate by treatment with potassium hydroxide gave a 50 per cent yield of phenylstearic alcohol, based on the oleyl acetate originally used.

Reaction of vinyl acetate with benzene in the presence of aluminum chloride has been claimed to yield β-phenylethyl acetate [98]:

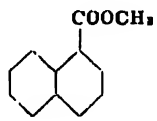
$$CH_3.COOCH:CH_2 + C_6H_6 \xrightarrow{AlCl_3} CH_3.COOCH_2.CH_2C_6H_5$$

Condensation products are analogously secured from vinyl esters and phenols.[99]

Addition of benzene at the double bond occurs in the formation of methyl 4-phenyl-4,5-dihydro-2-methyl-3-furoate from methyl 2-methyl-3-furoate:



Similar treatment of methyl 2-furoate, however, results in the production of methyl α-naphthoate,[100]



The formation of naphthoic acid ester may occur through an endoxy-compound as a result of 1,4-addition.[101]

Unsaturated Ketones and Aromatic Compounds

Aromatic hydrocarbons or phenol ethers add to ketene with formation of arylalkyl ketones:

$$CH_2:CO + RH \xrightarrow{AlCl_3} CH_3COR$$

The reaction was first studied by Hurd,[102] who secured rather unsatisfactory results, obtaining with benzene or anisole only complex mixtures from which he was able to isolate small amounts of ketones. With naphthalene, he secured a 20-37 per cent yield of a mixture of α- and β-acetonaphthones.

[98] German P. 666,466 (1938) to H. Hopff (to I. G.); *C. A.*, 33, 2149.
[99] French P. 675,668 (1929) to I. G.; *C. A.*, 24, 2758.
[100] M. McCorkle and J. A. V. Turck, Jr., *Proc. Iowa Acad. Sci.*, 43, 205-206 (1936); *C. A.*, 32, 4161.
[101] H. Gilman, M. McCorkle, and N. O. Calloway, *J. Am. Chem. Soc.*, 56, 745 (1934).
[102] C. De W. Hurd, *J. Am. Chem. Soc.*, 47, 2777-2780 (1925); *C. A.*, 20, 42.

An attempt to improve the technic was made by Ploeg,[103] who used the more active veratrole as the aromatic component, and passed hydrogen chloride through the solution during the passage of ketene. The expected product, 3,4-dimethoxyacetophenone, was secured in very low yield as the *p*-nitrophenylhydrazone.

Subsequent study of the reaction with benzene revealed the presence of *p*-ethylacetophenone, as well as acetophenone, in the reaction mixture.[104] The former product is probably formed from ethylene present in ketene.

A 32-37 per cent yield of acetophenone has been secured by Williams and Osborn.[105] These investigators stress the importance of the following factors:

(1) Use of a considerable excess of ketene.
(2) Use of ketene which contains a minimum amount of ethylene
(3) Operation at 0°.
(4) Use of a diluent, such as carbon disulfide.
(5) Addition of aluminum chloride in small portions with rapid stirring.

Williams and Osborn also report that the reaction of ketene and naphthalene can be so run that methyl α-naphthyl ketone in 34 8 per cent yield, is obtained to the practical exclusion of the β-isomer. These investigators secured a 24 1 per cent yield of methyl β-tetrahydronaphthyl ketone from tetralin and ketene, and a 23.4 per cent yield of *p*-phenylacetophenone from biphenyl and ketene.

Addition of benzene to mesityl oxide in presence of aluminum chloride occurs with production of β-phenylisobutyl methyl ketone:

$$CH_3CO.CH:\overset{\displaystyle CH_3}{\overset{|}{C}}.CH_3 + C_6H_6 \xrightarrow{AlCl_3} CH_3CO.CH_2.\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle C_6H_5}{\underset{|}{C}}}}-CH_3$$

Reaction occurs readily when 50 g of the oxide is added during the course of one hour to a mixture consisting of 90 g of aluminum chloride in 200 cc of benzene at 0°; stirring is continued for three hours longer. About 80 per cent of the theoretical yield of the saturated ketone is secured.[106]

Reaction of vinyl methyl ketone with naphthalene in presence of aluminum chloride has been claimed to give γ-ketobutylnaphthalene.[107]

Benzalacetophenone adds with benzene to yield β,β-diphenylpropiophenone:

$$C_6H_5CH:CHCOC_6H_5 + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_2CHCH_2COC_6H_5$$

[103] W. Ploeg, *Rec. trav. chim.*, 45, 342-344 (1926); *C. A.*, 20, 2321; *C. Z.*, 1926, I, 3393.
[104] K. Packendorff, N. D. Zelinski, and L. Leder-Packendorff, *Ber.*, 66, 1069-1073 (1933); *Brit. Chem. Abs.*-A, 1051 (1933). F. S. Spring and T. Vickerstaff, *J. Chem. Soc.*, 1673-1674 (1935).
[105] J. W. Williams and J. M. Osborn, Paper presented to the Division of Organic Chem., Am. Chem. Soc., Boston, 1939.
[106] A. Hoffman, *J. Am. Chem. Soc.*, 51, 2542-2547 (1929). E. Bergmann, H. Taubadel, and H. Weiss, *Ber.*, 64, 1493-1501 (1931).
[107] German P. 566,406 (1933) to H. Hopff (to I. G.); *C. A.*, 33, 2149.

When reaction is effected by adding 120 g of the unsaturated ketone in 300 cc of benzene during 30 minutes to a suspension of 160 g of aluminum chloride in 1700 cc of benzene at 10-20°, and stirring is continued for about one hour, 76-85 per cent of the theoretical yield of β,β-diphenylpropiophenone (m.p. 91-92°) is secured.[108]

According to Vorländer and Friedberg,[109] the addition of benzene to benzalacetophenone probably proceeds by intermediate formation of a hydrogen chloride addition product. They base their assumption on the fact that benzalmenthone similarly gives diphenylmethylmenthone, $C_{10}H_{17}O.CH(C_6H_5)_2$, and that benzalacetophenone and benzalmenthone form stable hydrochlorides. On the other hand, anisalacetophenone, $4\text{-}CH_3O.C_6H_4CH{:}COC_6H_5$, whose hydrochloride is very unstable, was found not to combine with benzene and aluminum chloride. A further confirmation of the formation of such a complex was found in the ready reaction of benzalacetophenone hydrochloride with benzene and aluminum chloride to give an excellent yield of β,β-diphenylpropiophenone. This product may also be secured by primary formation of a benzenesulfinic acid addition compound of benzalacetophenone. When a mixture of benzene, sulfur dioxide, and aluminum chloride and benzalacetophenone are reacted for about ten minutes, addition occurs probably according to the scheme:

$$C_6H_5CH:CHCOC_6H_5 + C_6H_6 + SO_2 \xrightarrow{AlCl_3} C_6H_5CH(O{-}S(=O){-}C_6H_5)CH_2COC_6H_5$$

Upon heating the addition compound with benzene and aluminum chloride for six hours, the $C_6H_5SO_2$ radical is exchanged by the phenyl group, and β,β-diphenylpropiophenone is obtained. Anisalacetophenone similarly forms a benzenesulfinate upon treatment with benzene, sulfur dioxide, and aluminum chloride, but an analogous replacement of the $C_6H_5SO_2$ group does not take place.

The addition of aryl groups to compounds in which an olefinic group is conjugated with a carbonyl group has been shown to be a reversible reaction. Reactions of this type are, therefore, further treated under the review of work which has been done on the reversibility of the Friedel-Crafts reaction.*

An interesting reaction is that of acetylketene with benzene and aluminum chloride to give a 10.5 per cent yield of benzoylacetone[110]:

$$C_6H_6 + CH_2COCH:CO \xrightarrow{AlCl_3} C_6H_5COCH_2COCH_3$$

[108] P. R. Shildneck, *Org. Syntheses*, 17, 51-53 (1937).
[109] D. Vorländer and A. Friedberg, *Ber.*, 56, 1144-1150 (1923); *C. A.*, 17, 3179.
* See page 483.
[110] C. D. Hurd and C. D. Kelso, *J. Am. Chem. Soc.*, 62, 1548-1549 (1940).

Addition of Aromatic Hydrocarbons or their Derivatives to Unsaturated Acid Chlorides

Kohler, Heritage, and Burnley [111] report that the Friedel-Crafts reaction of cinnamoyl chloride with benzene proceeds according to the schemes:

$$\text{(I)}\quad C_6H_5CH:CHCOCl + 2C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_2CHCH_2COC_6H_5 + HCl$$

$$\text{(II)}\quad C_6H_5CH:CHCOCl + C_6H_6 \xrightarrow{AlCl_3} \begin{array}{l} H \\ C{-}C_6H_5 \\ CH_2 \\ C \end{array} + HCl$$

In their experiment they also secured some β,β-chlorophenylpropiophenone. This may be assumed to be formed by hydrohalogenation during the reaction:

$$C_6H_5CH:CHCOCl \xrightarrow{C_6H_6 + HCl + AlCl_3} C_6H_5{-}\underset{Cl}{CH}\ CH_2COC_6H_5$$

McKenzie and Barrow [112] found that in an excess of benzene as diluent the reaction gives a mixture of β,β-diphenylpropionic acid and β,β-diphenylpropiophenone. In the production of the former, only addition at the double bond had occurred:

$$C_6H_5CH:CHCOCl \xrightarrow{C_6H_6 + AlCl_3} (C_6H_5)_2CH\ CH_2COCl \xrightarrow{H_2O}$$

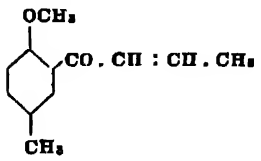
$$(C_6H_5)_2CH.CH_2COOH$$

Kohler and his co-workers [111] have pointed out that the reaction takes an entirely different course with phenol ethers. Whereas in the reaction of cinnamoyl chloride with hydrocarbons there is always addition at the ethylenic linkage, when diphenyl ether is used, only replacement of halogen occurs:

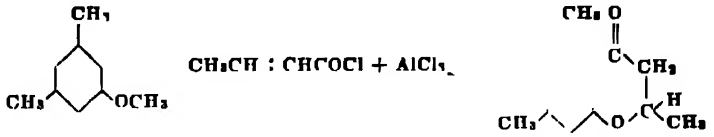
$$C_6H_5CH:CHCOCl \xrightarrow{C_6H_5\cdot O\cdot C_6H_5 + AlCl_3} C_6H_5CH:CHCOC_6H_4OC_6H_5 + HCl$$

Ring closure during Friedel-Crafts reaction of unsaturated acid chlorides with phenols or phenol ethers has been intensively investigated by von Auwers and his co-workers [113] It was found that by the action of crotonyl chloride on *p*-cresol methyl ether even in the presence of 2 moles of aluminum chloride, no ring closure occurred; there was secured *o*-propenyl *p*-cresyl ketone,

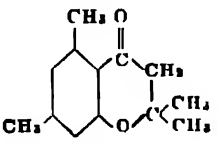
[111] E. P. Kohler, G. L. Heritage, and M. C. Burnley, *Am. Chem. J.*, 44, 60-76 (1910). *C. Z.*, 1910, II, 870-872.
[112] A. McKenzie and F. Barrow, *J. Chem. Soc.*, 119, 69-76 (1921).
[113] K. von Auwers and E. Lammerhirt, *Ann.*, 42, 1-58 (1920); K. von Auwers and H. Schutte, *ibid*, 59-86. K. von Auwers and R. Doll, *ibid*, 86-106. K. von Auwers, *ibid*, 106-118.



Reaction of *p*-cresol methyl ether with β,β-dimethylacrylic acid chloride yields *o*-isobutenyl *p*-cresyl ketone. Here, too, addition does not occur at the double bond. 3,5-Xylenol methyl ether with crotonyl chloride gives 2,5,7-trimethylchromanone:



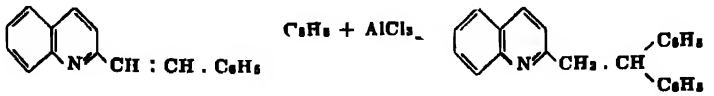
Here ring closure occurs with intermediate saponification of the methoxy- group, and addition of the hydroxy- group at the double bond of the intermediately formed unsaturated ketone. An analogous condensation occurs when β,β-dimethylacrylyl chloride is substituted for crotonyl chloride, the product secured being 2,2,5,7-tetramethylchromanone:



Reactions of unsaturated acid chlorides with aromatic compounds have also been discussed in the section dealing with ketone synthesis.*

Reversibility of the Friedel-Crafts Reaction with Olefins Having Conjugated Double Bonds

Reaction of benzalquinaldine with benzene in presence of aluminum chloride takes the expected course, with production of α-benzohydrylquinaldine [114]:

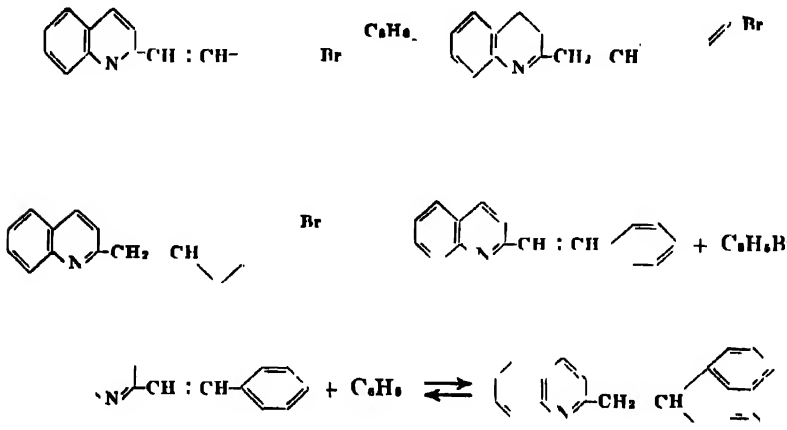


With *p*-chlorobenzalquinaldine, however, the reaction takes an anomalous course, for here, the chlorine-free α-benzohydrylquinaldine is formed. The same product was also secured with *p*- or *m*-bromobenzalquinaldine. That removal of halogen was not due to the action of aluminum chloride

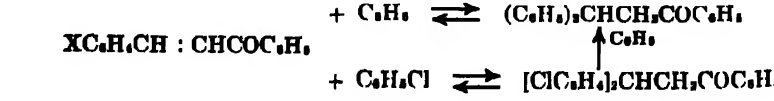
* See pages 212, 242 and 248.

[114] A. Hoffmann, M. W. Farlow, and R. C. Fuson, *J. Am. Chem. Soc.*, 55, 2000-2004 (1933).

alone was shown by the fact that *p*-chlorobenzalquinaldine was not sensitive to the action of aluminum chloride. Further investigation [115] showed that during the reaction the entire halophenyl radical is replaced by an unsubstituted phenyl group. Experiments with *p*-bromobenzalquinaldine revealed bromobenzene as a reaction product. The course of the condensation is reversible:



Analogously, it has been shown that benzallepidine and *p*-chlorobenzallepidine react with benzene in the presence of aluminum chloride and hydrogen chloride to give α-benzohydryllepidine.[110] The same course was taken in the reaction of *o*- or *p*-chlorocinnamic acid with benzene or chlorobenzene. In each case cleavage of a halophenyl from the primary condensation product occurred. A reversible reaction was also found to occur with substituted benzalacetophenones [117] Benzalacetophenones in which the substituent (X) was *o*-, *m*-, or *p*-chlorine, *m*- or *p*-bromine, or *p*-methyl were found to react with benzene, aluminum chloride, and hydrogen chloride to give one product, β,β-diphenylpropiophenone:



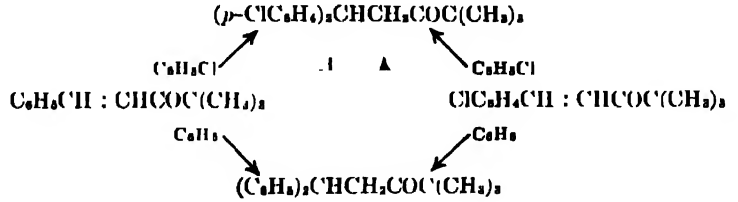
Condensation of chlorobenzene with benzalacetophenones of the same type also gave one product, β,β-bis(*p*-chlorophenyl)propiophenone. The reversibility of the reaction was further substantiated by the fact that treatment of β,β-bis(*p*-chlorophenyl)propiophenone with benzene and aluminum chloride gave a 30 per cent yield of β,β-diphenylpropiophenone

[115] R. C. Fuson, A. P. Kosacik, and J. T. Eaton, *J. Am. Chem. Soc.*, **55**, 3799-3803 (1933).
[116] R. C. Fuson, L. L. Alexander, E. Ellingboe, and A. Hoffmann, *J. Am. Chem. Soc.* **58**, 1978-1980 (1936).
[117] J. T. Eaton, D. B. Black, and R. C. Fuson, *J. Am. Chem. Soc.*, **56**, 887-888 (1934).

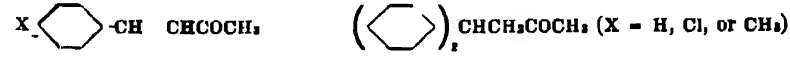
β,β-Diarylcarbonyl compounds of the type $(Ar)_2CHCH_2CO-$ were also found to be interconvertible according to the equation:

$$(Ar)_2CHCH_2CO- + 2Ar'H = (Ar')_2CHCH_2CO- + 2ArH$$

This was shown with α-(benzohydryl)pinacolones. In the presence of hydrogen chloride, benzene reacts with benzal-, *p*-chlorobenzal-, or *o*-chlorobenzalpinacolone to yield α-(benzohydryl)pinacolone. With chlorobenzene instead of benzene the product in each case is α-(*p,p'*-dichlorobenzohydryl)pinacolone. That the reaction is reversible is evident from the fact that under the same conditions chlorobenzene converts α-(benzohydryl)pinacolone into α-(*p,p'*-dichlorobenzohydryl)pinacolone, and that the latter is changed to the former when benzene replaces chlorobenzene in the reaction mixture [118]:



The reversibility of the Friedel-Crafts reaction in the case of addition of aromatic compounds to an olefinic linkage which is conjugated with a carbonyl group was further demonstrated in the conversion of benzalacetone or its *p*-methyl or *p*-chloro- derivatives by treatment with benzene in the presence of aluminum chloride into benzohydrylacetone in yields of 59, 92, and 68 per cent, respectively.



Benzohydrylacetones, dibenzalacetones, and benzohydrylmethyl styryl ketones were similarly transformed into the corresponding unsubstituted benzohydryl compounds. In these reactions, intermediate products were isolated.[119]

Reversible reaction together with hydrogenation occurs in reactions effected with 1,1-diaryl-2-acylethylenes.[120] The ketones are hydrogenated to the corresponding saturated diaryl ketones:

$$(Ar)_2C : CHCOR \xrightarrow{C_6H_6 + AlCl_3} (Ar)_2CHCH_2COR$$

Hydrogenation of this type was found to occur upon treatment of β-(*p*-chlorophenyl)cinnamic acid or 1,1-bis(*p*-chlorophenyl)-2-benzoylethylene with benzene and aluminum chloride. The products were β,β-diphenylpropionic acid or α-benzohydrylacetophenone, respectively.

[118] H. Weinstock, Jr., and R. C. Fuson, *J. Am. Chem. Soc.*, **56**, 1241-1242 (1934).
[119] C. F. Woodward, G. T. Borcherdt, and R. C. Fuson, *J. Am. Chem. Soc.*, **56**, 2103-2105 (1934).
[120] L. L. Alexander, A. L. Jacoby, and R. C. Fuson, *J. Am. Chem. Soc.*, **57**, 2208-2209 (1935).

Hydrogenation was also observed in the conversion of 1,1-diphenyl-2-benzoylethylene and 1,1-diphenyl-2-trimethylacetylethylene into α-benzohydrylacetophenone and α-benzohydrylpinacolone, respectively. That exchange of an aryl group also occurs is shown in the conversion of stilbene, *p*-bromostilbene, and *p,p'*-dichlorostilbene into bibenzyl, according to the general reaction:

$$XC_6H_4CH:CHC_6H_4X + 2C_6H_6 + 2H \xrightarrow{AlCl_3} C_6H_5CH_2CH_2C_6H_5 + 2C_6H_5X$$

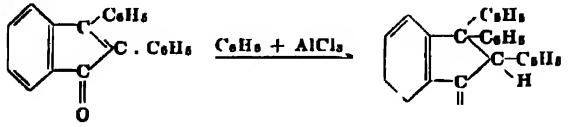
A 70 per cent yield of bibenzyl was secured from *p,p'*-dichlorostilbene

Bibenzyl, in the indicated yields also has been secured by treatment of the following ethylene and acetylene derivatives with benzene, aluminum chloride, and hydrogen chloride[121]:

Material treated	% yield of bibenzyl
Tolane	32
Triphenylethylene	28
1,1-Bis(*p*-chlorophenyl)-2-phenylethylene	27
1,1,2-Triphenylethane	57
sym-Tetraphenylethane	54

The formation of bibenzyl by the action of benzene and aluminum chloride has been described as a general phenomenon for acetylene and ethylene derivatives in which each carbon atom bears at least one aryl group, and for similarly constituted tri- and tetraarylethanes The addition of hydrogen to the double bond is obviously irreversible, whereas the addition of aromatic hydrocarbons is reversible.

Addition of benzene at the double bond occurs upon boiling diphenylindone with 2 moles of aluminum chloride in an excess of benzene.

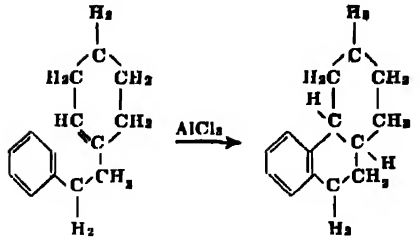


2,3,3-Triphenylhydrindone is thus secured in excellent yield.[122] That the reaction occurs through reversible addition was shown by the fact that 2,3,3-triphenylhydrindone may also be obtained from 2-phenyl-3-*p*-tolylindone, benzene, and aluminum chloride in a similar yield.

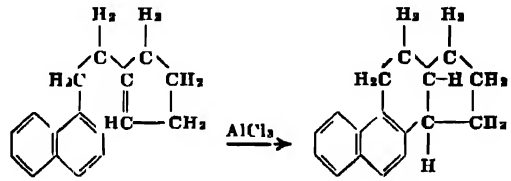
Intramolecular Ring Closure of Arylalkyl Unsaturated Compounds

Isomerization of alicyclic olefins having arylalkyl substituents adjacent to the double bond occurs upon treatment with aluminum chloride to give ring closure by addition of the aromatic residue at the double bond of the alicyclic olefin:

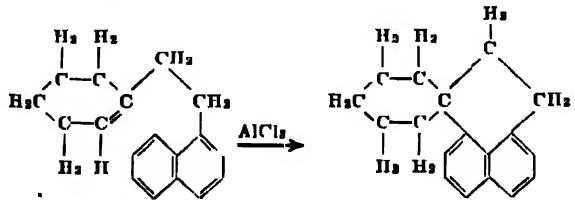
[121] L. L. Alexander and R. C. Fuson, *J. Am. Chem. Soc.*, **58**, 1743-1747 (1936)
[122] C. F. Koelsch, *J. Org. Chem.*, **3**, 456-461 (1938).



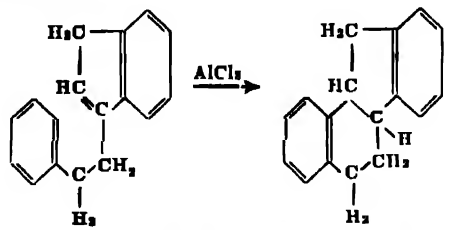
The cyclization shown above has been effected by adding 4 g of aluminum chloride to a solution of 2.8 g of 1-β-phenylethyl-Δ^1-cyclohexene in 30 cc of carbon disulfide and allowing the mixture to stand for 24 hours. There was obtained 1.4 g of 1,2,3,4,9,10,11,12-octahydrophenanthrene.[123] Mild conditions suffice for the cyclization of 1-(β-1′-naphthylethyl)-Δ^1-cyclopentene to 1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene[124]:



Treatment of 35 g of 1(β-1′-naphthylethyl)-Δ^1-cyclohexene in 350 cc of carbon disulfide with 42 g of aluminum chloride with cooling gives 7,8-dihydrophenalyl-7-spirocyclohexane[125]:

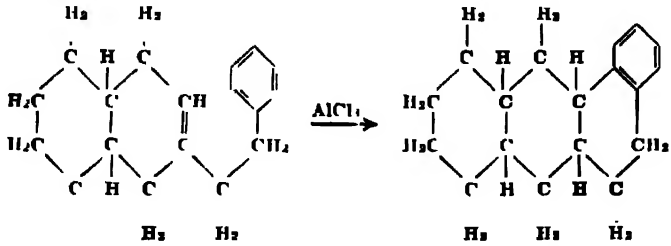


3-β-Phenylethylindene shows considerable resistance to cyclization, for only a small yield of tetrahydrochrysofluorene is secured by treatment with aluminum chloride[125]:

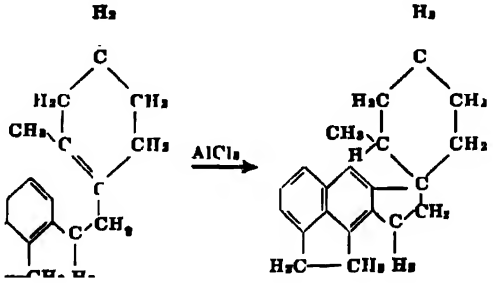


[123] J. W. Cook and C. L. Hewett, *J. Chem. Soc.* 1098-1111 (1933). J. W. Cook and G. A. D. Haslewood, *J. Chem. Soc.*, 767-770 (1935).
[124] J. W. Cook and C. L. Hewett, *loc. cit.*
[125] J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 365-377 (1934); *C. A.*, 28, 3413.

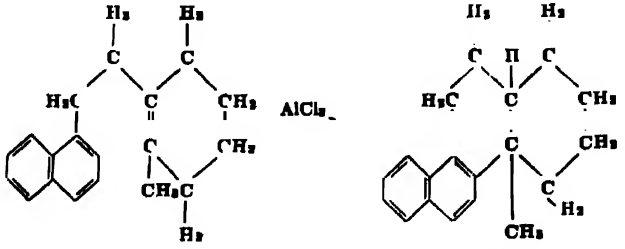
Ring closure of 2-β-phenylethyl-Δ^2-octalin yields dodecahydro-1,2-benzanthracene [125]:



Cyclization of 2-methyl-(β-1'-acenaphthylethyl)-Δ^1-cyclohexene gives an inseparable mixture of hydrocarbons, one of which is considered to be the spiran [126]:

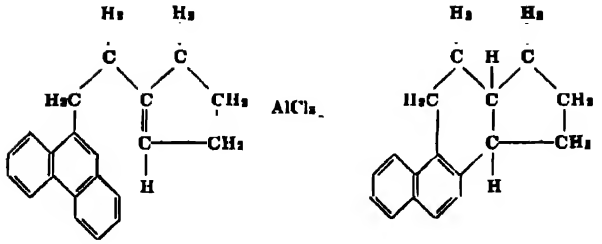


Since the presence of the methyl group in cyclohexene interfered with six-membered ring closure, the effect of the methyl group on cyclization of 2-methyl-(β-1'-naphthylethyl)-Δ^1-cyclohexene was investigated In this case, six-membered ring closure was secured, the product being methyloctahydrochrysene:

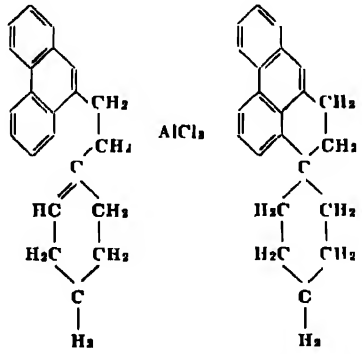


According to Bergmann and Blum-Bergmann,[127] aluminum chloride cyclization of 1-(β-9'-phenanthrylethyl)-Δ^1-cyclopentene gives tetrahydrocyclopentanotriphenylene:

[125] J. W. Cook, G. A. D. Haslewood, and A M Robinson, *J. Chem. Soc*, 967-971 (1935)
[126] E. Bergmann and O. Blum-Bergmann, *J Am Chem Soc*, 58, 1678-1681 (1936)

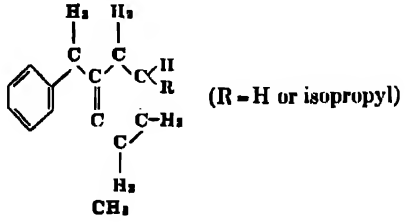


More recently, however, Hewett[128] has found that the analogous cyclohexene compound, 1-(β-9′-phenanthrylethyl)-Δ¹-cyclohexene cyclizes to give the spiran, probably dihydrobenzophenanthrenespirocyclohexane:



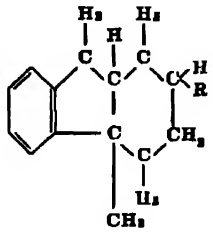
Hewett suggests that the compound secured by Bergmann and Blum-Bergmann is likewise a spiran.

Attempts to cyclize 1-benzyl-Δ¹-cyclohexene by treatment with aluminum chloride leads mainly to polymerization. Under like conditions, however, treatment of the substituted benzylcyclohexenes of the type

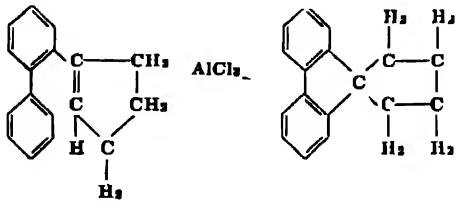


with aluminum chloride at 0° gives good yields of corresponding hydrofluorene derivatives[129]:

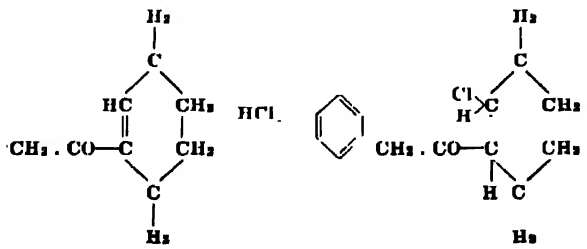
[128] C. L. Hewett, *J. Chem. Soc.*, 196-196 (1938).
[129] J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 62-71 (1936).



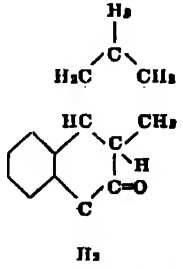
A spiran is secured in the cyclization of 1-(*o*-biphenyl)-Δ^1-cyclopentene [130]:



Cook and Hewett [131] have been unable to cyclize phenylacetylcyclohexene to hexahydrophenanthrene, and they have attributed their failure to the inhibiting influence of the conjugated carbonyl group on the activity of the ethylenic bond. Nenitzescu and Gavat [132] advance the formation of a hypothetical chloro- compound formed by the action of aluminum chloride on the unsaturated ketone, probably according to

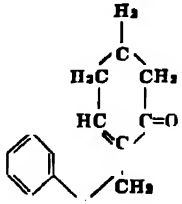


Such a chloro- compound should yield

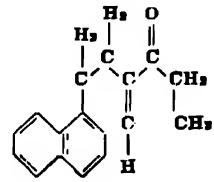


[130] W. E. Bachmann and M. C. Kloetzel, *J. Am. Chem. Soc.*, **59**, 2207-2213 (1937).
[131] J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 1098-1111 (1933).
[132] C. D. Nenitzescu and I. Gavat, *Ann.*, **519**, 260-271 (1935).

The failure to secure ring closure of this type has been suggested by Nenitzescu and Gavat to be due to a migration of the chlorine in the intermediate compound, similar to that observed by these investigators in the conversion of 1-chloro-2-acetylcyclohexane into 5-chloro-2-acetylcyclohexane during reaction of the former with benzene in presence of aluminum chloride. Halogen migration during attempted ring closure of phenylacetylcyclohexene would thus inhibit expected cyclization. Cohen and Cook [133] were unable to accept such an explanation of their failure to effect the ring closure; for if it were correct, it would be necessary further to postulate a *reversible* migration to account for the isolation of unchanged ketone after treatment with aluminum chloride. That the conjugated carbonyl group exerted a suppression of anionoid reactivity of an ethylenic linkage was further demonstrated by the fact that neither 2-β-phenethyl-Δ^2-cyclohexenone (I) or 2(β-1′-naphthylethyl)-Δ^2-cyclopentenone (II) could be cyclized even by drastic treatment with aluminum chloride or sulfuric acid:



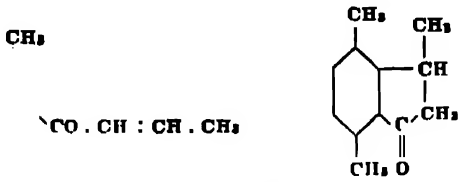
(I)



(II)

Harper [134] has reported that ketone (II) resists cyclization by phosphorus pentoxide.

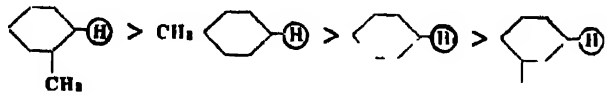
Unsaturated arylalkyl ketones having several alkyl substituents in the nucleus undergo cyclization upon treatment with aluminum chloride. Thus, 1,4-dimethyl-3-crotonylbenzene yields 3,4,7-trimethyl-α-hydrindone:



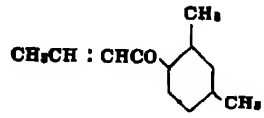
According to von Auwers and Risse,[135] who report the above reaction, ring closure of unsaturated arylalkyl ketones is inhibited when there is present a methyl group in the position *meta-* to the hydrogen of the ben-

[133] A. Cohen and J. W. Cook, *J. Chem. Soc.*, 1570-1572 (1935).
[134] S. H. Harper, *J. Chem. Soc.*, 1859 (1937).
[135] K. v. Auwers and E. Risse, *Ann.*, 502, 282-299 (1933).

zene ring which is to be displaced upon ring closure. The influence of the alkyl substituent upon the loosening of the hydrogen atom which is to be displaced is given:

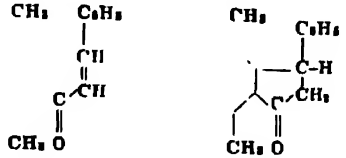


Thus, when 1,3-dimethyl-6-crotonylbenzene,

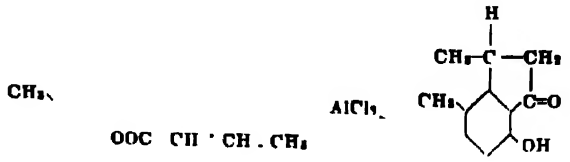


is heated with aluminum chloride, the main reaction appears to be one of polymerization rather than of ring closure Here the hydrogen does not become labile because of the retarding effect of the methyl groups in *m*- position.

Chalcones with activating methyl substituents may likewise undergo ring closure 2',5'-Dimethylchalcone yields 4,7-dimethyl-3-phenyl-α-hydrindone:



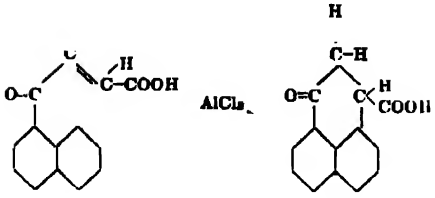
The rearrangement of *p*-cresyl crotonate by treatment with aluminum chloride results in formation of 3,4-dimethyl-7-hydroxyhydrindone [140]



Here a Fries rearrangement occurs with intermediate formation of unsaturated ketone, and ring closure occurs by addition at the double bond

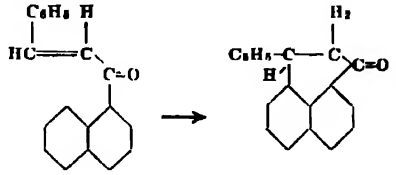
Cyclization of β-1-naphthoylacrylic acid is claimed to proceed according to the following scheme, the resulting acid melting at 186-187°:

[140] K v. Auwers and E Lammerhirt, *Ann*, 421, 1-59 (1920).



β-Acenaphthoylacrylic acid similarly undergoes cyclization.[137]

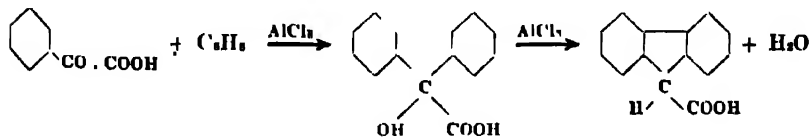
The production of 3-phenyl-*peri*-naphthindone, m.p. 151-152°, has been reported by cyclization of 1-cinnamoylnaphthalene with aluminum chloride in carbon disulfide, probably according to the reaction [138]:



The ring closure is claimed to be general with unsaturated ketones of the general formula, $1\text{-}C_{10}H_7COCR{:}CR_1R_2$ where R, R_1, and R_2 are hydrogen or aryl residues.

Addition to Arylglycolic Acids or Aldehydes

Fluorene carboxylic acids may be prepared by condensation of arylglycolic acids with benzene and aluminum chloride. Benzoylformic acid adds to benzene to yield benzilic acid, which during the reaction loses 1 mole of water to form fluorene-9-carboxylic acid:



Upon heating 6 g of benzoylformic acid with 140 cc of benzene and 12 g of aluminum chloride for two hours about 1 g of fluorene carboxylic acid is secured. When toluene is substituted for benzene in the above reaction, a slightly better yield of *p*-methylfluorenecarboxylic acid is secured.[139]

Arylglyoxals add to aromatic compounds in the presence of aluminum chloride to give mixed benzoins, according to the general equation:

$$RCOCHO + R'H \xrightarrow{AlCl_3} RCOCH(OH)R'$$

[137] British P. 278,821 (1927) to I. G.; *Brit. Chem. Abs.*-B, 887 (1928).
[138] German P. 491,089 (1930) to G. Kalischer, E. Honold, and H. Gremme (to I. G.); *C. A.*, 24, 2475.
[139] D. Vorländer and A. Pritsche, *Ber.*, 46, 1793-1796 (1913).

Fuson and his co-workers [140] first reported the reaction as a convenient method for the preparation of 2',4',6'-trimethylbenzoin. Upon addition, during two hours with stirring, of 17.6 g of mesitylglyoxal dissolved in 100 cc of benzene, and subsequent stirring of the reaction mixture for five hours at room temperature, there was obtained 16.1 g of crude 2',4',6'-trimethylbenzoin, m.p. 97-99°. The method was later [141] assumed to be of general applicability, the following benzoins being secured by reaction of the appropriate arylglyoxal and aromatic compound at 0° with aluminum chloride under the indicated reaction conditions:

Benzoin	m.p. (°C)	% Yield	Time (hrs)	Solvent
$C_6H_5COC(OH)HC_6H_5$	133	90	20	C_6H_6
$C_6H_5COC(OH)HC_6H_4OCH_3$	100	48	5	CS_2
$C_6H_5COC(OH)HC_{10}H_7$	128	42	15	CS_2
$C_6H_5COC(OH)HC_6H_4Cl$	116	84	15	CS_2
$ClC_6H_4COC(OH)HC_6H_5$	90–91	35	15	C_6H_6
$C_6H_5COC(OH)HC_6H_3(CH_3)_2$	93.5–94	62	5	CS_2
$(CH_3)_2C_6H_3COC(OH)HC_6H_5$	102–103	63	7	C_6H_6
$BrC_6H_4COC(OH)HC_6H_5$	108–109	70	15	C_6H_6
$C_6H_5COC(OH)HC_6H_4Br$	125–126	57	15	C_6H_5Br
$C_6H_5COC(OH)HC_6H_4CH_3$	116	50	15	CS_2
$CH_3C_6H_4COC(OH)HC_6H_5$	110	42	15	CS_2

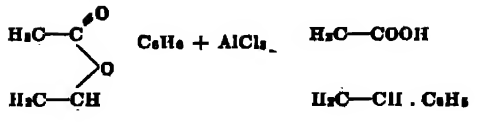
In all cases each reaction yielded only one benzoin.

Subsequent investigation,[142] however, has shown that steric hindrance prevents condensation of mesitylglyoxal with some tri- and tetra-substituted aromatic hydrocarbons. Reaction of benzene, toluene, *m*-xylene, or mesitylene with mesitylglyoxal and aluminum chloride in carbon disulfide solution gave 57, 24, 17, and 40 per cent yields of the corresponding benzoins, respectively. In the reaction with *m*-xylene, a 34 per cent yield of 2,4,6-trimethylbenzoyl-bis(2,4-dimethylphenyl)methane, produced by reaction of the primarily formed benzoin with additional *m*-xylene, was also obtained. If, instead of carbon disulfide, an excess of *m*-xylene was used as diluent, the only reaction product was the diarylaroylmethane. Reaction could not be effected with mesitylglyoxal and 1,3,5-triethylbenzene, durene, or isodurene. The more active 3,5-dimethylanisole or 3,5-dimethylphenetole, however, reacted very readily, with production of substituted diphenylbenzoylmethanes even in carbon disulfide solution

Reaction of Lactones and Phthalides with Aromatic Hydrocarbons

Addition of benzene to lactones of aliphatic monocarboxylic acids generally results in formation of aralkyl acids.

[140] R. C. Fuson, H. H. Weinstock, Jr., and G. E. Ullyot, *J. Am. Chem. Soc.*, **57**, 1803-1804 (1935)
[141] R. T. Arnold and R. C. Fuson, *J. Am. Chem. Soc.*, **58**, 1295-1296 (1936).
[142] R. C. Fuson, W. S. Emerson, and H. H. Weinstock, Jr., *J. Am. Chem. Soc.*, **61**, 412-413 (1939).



γ-methylbutyrolactone γ-methyl-γ-phenylbutyric acid

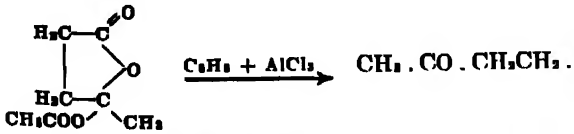
The reaction is similar to the synthesis of keto- acids from phthalic anhydride. It has been extensively studied by Eijkman, who secured γ-methyl-γ-phenylbutyric acid by reacting 30 g of γ-methylbutyrolactone with 60 g of benzene and 50 g of aluminum chloride. This investigator reports the following preparations:

Lactone	Hydrocarbon	Aralkyl Acid	Ref.
γ-Methylbutyro-	benzene	γ-methyl-γ-phenylbutyric	1
γ-Methylbutyro-	toluene	γ-methyl-γ-tolylbutyric	1
γ-Phenylbutyro-	benzene	γ,γ-diphenylbutyric	1
Phenylparaconic acid $C_6H_5CH\,CH(COOH).CH_2COO$	benzene	diphenylmethylsuccinic	2
" "	toluene	phenyltolylmethylsuccinic	2
" "	ethyl-benzene	(ethylphenyl)phenylmethyl-succinic	2
Hexylparaconic acid $C_6H_{13}.CH.CH(COOH).CH_2COO$	benzene	no reaction	3
γ-Cyanovalero- $CH_2.CHCN.CH_2.CH_2\,COO$	benzene	no reaction	3
α-Angelica- $CH_3.C:CH.CH_2.COO$	benzene	diphenylmethylbutyric	3
Campholide	benzene	phenylcampholic acid	4

References

1 J. F. Eijkman, *Chem. Weekblad*, 1, 421-424 (1904); *C. Z.*, 1904, I, 1416.
2 J. F. Eijkman, *Chem. Weekblad*, 2, 229-231 (1905); *C. Z.*, 1905, I, 1388.
3 J. F. Eijkman, *Chem. Weekblad*, 4, 727-738 (1907); *C. Z.*, 1907, II, 2045.
4. J. F. Eijkman, *Chem. Weekblad*, 4, 191-193 (1907); *J. Chem. Soc. Abs.*, 92 (I), 378 (1907).

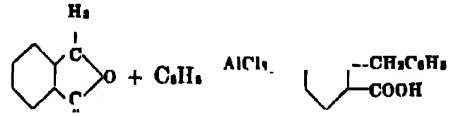
Addition of benzene to γ-acetoxy-γ-valerolactone in presence of 3 molecular equivalents of aluminum chloride at 45-50° results in a 60 per cent yield of phenacylacetone [143]:



[143] J. H. Helberger, *Ann.*, 522, 269-277 (1936); *Brit. Chem. Abs.*-A, 822 (1936).

Only a very small amount of the expected diphenylvaleric acid was secured. Obviously reaction had occurred primarily with formation of the normal acid chloride, $CH_3CO.CH_2CH_2COCl$.

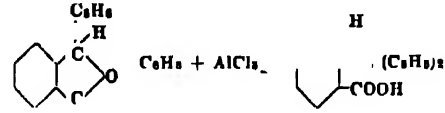
The condensation of phthalide with benzene in presence of aluminum chloride gives a 50 per cent yield of *o*-benzylbenzoic acid [144]:



With naphthalene in carbon disulfide solution, the product is 2-(β-naphthylmethyl)benzoic acid, obtained in only a small yield If the reaction is effected in benzene solution, no reaction with naphthalene takes place, preferential addition with only benzene occurring Coumarin and benzene with aluminum chloride gives only a small amount of β-phenyl-α,β-dihydrocoumarin, m.p. 82°. Here addition occurs only at the double bond, with no rupture of the coumarin ring Addition to the double bond also occurred upon similar treatment of coumarilic acid

The production of alkylaryl carboxylic acids by reaction of phthalide or chloro- or nitrophthalide, with toluene in the presence of aluminum chloride is claimed by Jaeger and Daniels [145]

In 1886, Gresly [146] reacted phenylphthalide with benzene in the presence of aluminum chloride and secured 2-(diphenylmethyl)benzoic acid



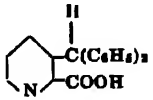
Addition of benzene to *p*-tolylphthalide was stated to occur analogously, with production of 2-(*p*-tolylphenylmethyl)benzoic acid, m.p. 154-155° According to Guyot,[147] however, the reaction product is really 2-(diphenylmethyl)benzoic acid. Guyot prepared 2-(*p*-tolylphenylmethyl)-benzoic acid (m.p. 172°) by addition of toluene to phenylphthalide in the presence of aluminum chloride.

It has been reported that addition of benzene to diphenylphthalide in presence of aluminum chloride cannot be effected.[144]

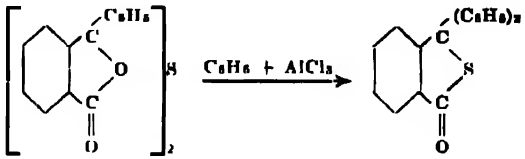
Attempts have been made to extend the reaction to organic compounds of nitrogen and of sulfur. According to Jephcott,[148] phenylpyridophthal-

[144] E. J. King, *J. Am. Chem. Soc.*, 562-566 (1927), *C. A.*, 21, 911; E. J. King, *Trans. Roy. Soc. Can. III (3)*, 19, 29 (1925), *C. A.*, 20, 751.
[145] U. S. P. 1,991,960 (1935) to A. O. Jaeger and L. C. Daniels (to American Cyanamid and Chemical Corp.); *C. A.*, 29, 479; *Brit. Chem. Abs.*-B, 940 (1935).
[146] L. Gresly, *Ann.*, 234, 241-243 (1886).
[147] A. Guyot, *Bull. soc. chim. (3)*, 17, 966-982 (1897); *C. Z.*, 1898, I, 311.
[148] C. M. Jephcott, *J. Am. Chem. Soc.*, 50, 1189-1192 (1928).

ide and benzene gives a 25-30 per cent yield of *o*-(diphenylmethyl)picolinic acid,



Recently, O'Brochta and Lowy [149] reported the production of thiodiphenyl phthalide by reaction of diphenyldiphthalidyl sulfide with benzene and aluminum chloride:



Addition of Acetylene to Aromatic Compounds

In 1887, Varet and Vienne [150] reported that by passing a current of acetylene for five hours per day during 10 days into a mixture consisting of 200 g of benzene and 50 g of aluminum chloride, a product consisting of 80 parts of styrene (b.p. 143-145°), 15 parts of diphenylethane (b.p. 265-270°), and 5 parts of bibenzyl (b.p. 280-286°) was secured. Reaction was effected by gently heating the liquid only at the beginning of each treatment; afterwards the heat developed by the reaction itself was sufficient.

The reaction of nascent acetylene with benzene in the presence of aluminum chloride has been studied by Parone.[151] To a layer of water about 1 cm in height, there was added 50 g of crystallized benzene (b.p. 80-81°), and to this calcium carbide was carefully added in such a manner that it did not remain in contact with the benzene. As soon as the first bubbles of acetylene had appeared, aluminum chloride was added. The reaction was allowed to continue for several days, during which time the water, the aluminum chloride, and the calcium chloride were frequently renewed. At the end of the reaction the upper layer was washed with water, filtered, and distilled over lime. The distillate was separated into the following fractions:

80-100°
100-135°
135-145°
145-150°
150-250°
250-300°
300-360°

[149] J. O'Brochta and A. Lowy, *J. Am. Chem. Soc.*, 61, 2765-2768 (1939).
[150] R. Varet and G. Vienne, *Bull. soc. chim. (2)*, 47, 917-919 (1887); *Compt. rend.*, 104, 1375-1377 (1887); *J. Chem. Soc. Abs.*, 52, 906 (1887).
[151] E. Parone, *L'Orosi*, 25, 148-153 (1902); *J. Chem. Soc. Abs.*, 86 (I), 26 (1904); *C. Z.*, 1903, II, 1662.

Besides the unchanged benzene, ethylbenzene as the main product, together with styrene, bibenzyl, and anthracene, were secured.

The condensation of acetylene with benzene and its derivatives in the presence of aluminum chloride was subsequently studied by Cook and Chambers.[152] In spite of the fact that the experimental procedure of Varet and Vienne was followed as closely as possible, these investigators could not duplicate the results. Only traces of styrene were secured They found the normal course of the reaction of acetylene with benzene to consist in the union of 2 moles of benzene with 1 mole of acetylene to form diphenylethane,

$$2C_6H_6 + CH \vdots CH \xrightarrow{AlCl_3} C_6H_5CH_2 . CH_2C_6H_5$$

and subsequent reaction of the diphenylethane with more acetylene to yield anthracene. Formation of products with ethylenic double bonds did not occur in reactions with toluene or with chlorobenzene. Phenol, methyl benzoate, and aniline, united with the aluminum chloride in molecular proportions, and did not react further. No reaction occurred with nitrobenzene, acetylene, and aluminum chloride.

The action of acetylene on benzene in presence of aluminum chloride was further studied by Böeseken and Adler.[153] Experiments carried out with an Al-$HgCl_2$ catalyst gave a small quantity of an oil (b.p. 265-285°/760 mm), which behaved like the reaction product described by Cook and Chambers.[152] With aluminum chloride prepared from aluminum and hydrogen chloride, the reaction was very slow. An active catalyst was secured only from aluminum and dry chlorine. On passing acetylene at about 20° during five hours through a mixture of 110 cc of benzene and 30 g of aluminum chloride, they obtained a reaction product consisting of 50 cc of benzene and 65 g of a bright-yellow powder, insoluble in all solvents, having the composition $(CH)_n$. By distilling the powder in cathode vacuum at 310°, a small amount of styrene was secured. Styrene, however, does not form either a polymerization or a depolymerization product which corresponds to the product, $(CH)_n$, obtained. Böeseken and Adler conclude that under the influence of the aluminum chloride a molecular compound, C_8H_8, is formed. This was given the name protostyrene. By distillation in high vacuum of this compound, some styrene was recovered. In order to determine if the compound $(CH)_n$ were merely a polymerization product of acetylene, attempts were made to polymerize acetylene by aluminum chloride in other solvents, but these were unsuccessful. The triple-bonded acetylene was obviously more difficultly polymerized than the product secured from benzene and acetylene. In this connection it is of interest that Berthelot[154] has reported that the thermal polymerization of acetylene yields a liquid which contains 20 per cent of styrene, and that polymerization products of acetylene, resembling cuprene, have been claimed

[152] O. W. Cook and V. J. Chambers, *J. Am. Chem. Soc.*, 43, 334-340 (1921); *C. A.*, 15, 1526.
[153] J. Böeseken and A. A. Adler, *Rec. trav. chim.*, 48, 474-485 (1929); *C. A.*, 23, 2948.
[154] M. Berthelot, *Ann.*, 141, 173-184 (1867).

to be formed upon passing acetylene at 90° through a mixture of benzene and aluminum chloride.[155] When Böeseken and Adler[153] reacted acetylene with chlorobenzene and aluminum chloride, polychlorostyrene was secured. Since chlorobenzene is less reactive than benzene, protochlorostyrene, the initial product of the condensation, probably had time to pass into chlorostyrene, which then condensed further to polychlorostyrenes. The reaction product secured from chlorobenzene, therefore, was soluble in organic solvents, was of low molecular weight, and gave no chlorostyrene upon distillation.

The temperature of reaction has been shown to have a great influence on the reaction of acetylene with benzene in the presence of aluminum chloride.[156] Lower temperatures give less oily and resinous substances and more insoluble solids. At higher temperatures no insoluble solids are formed, the product consisting of oily compounds and soluble resins. Reaction at higher temperatures and stopping at an intermediate stage gives mostly oily products. These were found to consist of alkylated benzenes and various arylated paraffins.

It has been reported[157] that acetylene does not appear to react with naphthalene at 100-200° in the presence of aluminum chloride.

Addition of phenyldichloroarsine to acetylene in the presence of aluminum chloride leads to production of a mixture of β-chlorovinylphenylchloroarsine, β,β'-dichlorodivinylphenylarsine, and β-chlorovinyldiphenylarsine.[158] The entire reaction probably proceeds as follows:

$$4C_6H_5 . AsCl_2 + 4CH \equiv CH \xrightarrow{AlCl_3} C_6H_5 . AsCl . CH : CHCl +$$

$$C_6H_5 . As(CH : CHCl)_2 + (C_6H_5)_2As . CH : CHCl + AsCl_3$$

Alkylation of Aromatic Hydrocarbons with Paraffins and Cycloparaffins

When paraffins of more than four carbon atoms are reacted with aromatic hydrocarbons in the presence of aluminum chloride, cleavage of the paraffin with subsequent addition of the cleaved fragment to the aromatic hydrocarbons occurs. 2,2,4-Trimethylpentane reacts readily with benzene in the presence of aluminum chloride and hydrogen chloride at 25-50° during about four hours under ordinary pressure to first give *tert*-butylbenzene and isobutane, which then react with each other to give di-*tert*-butylbenzene.[159] The reaction has been shown to be applicable to a number of paraffinic hydrocarbons ranging from pentanes to *n*-hexadecane.[160]

[155] U. S. P. 1,810,174 (1931) to W. O. Herrmann, H. Deutsch, and W. Haenel (to Consortium f. Elektrochem. Industrie); *C. A.*, 25, 4726; Fr. P. 593,388 (to Consortium f. Elektrochem. Industrie); *C. Z.*, 1926, II, 1791.
[156] R. Nodzu and R. Kan Ei, *J. Chem. Soc. Japan*, 59, 1304-1310 (1938), *C. A.*, 33, 2131
[157] F. Fischer and W. Schneider, *Ges. Abhandl. zur Kenntnis der Kohle*, 1917 (1), 227-230; *C. A.*, 13, 3183 (1919).
[158] H. N. Das-Gupta, *J. Indian Chem. Soc.*, 14, 349-353 (1937); *C. A.*, 31, 7423; *C. Z.*, 1938, I, 596.
[159] A. V. Grosse and V. N. Ipatieff, *J. Am. Chem. Soc.*, 57, 2415-2419 (1935); *C. A.*, 30, 1751.
[160] A. V. Grosse, J. M. Mavity, and V. N. Ipatieff, *J. Org. Chem.*, 3, 137-145 (1938).

The mechanism assumed for the reaction is as follows:

$$(a)\quad RH' + HCl \xrightarrow{AlCl_3} RCl + R'H$$

$$(b)\quad RCl + ArH \xrightarrow{AlCl_3} ArH + HCl$$

The course of the reaction with the individual paraffins was found to depend upon the manner in which the paraffin decomposes. 2,2,3-Trimethylpentane, like 2,2,4-trimethylpentane noted above, is ruptured at only one point. Both hydrocarbons react with benzene to yield *tert*-butylbenzene, 2,2,3-trimethylpentane reacting according to the scheme

$$(CH_3)_3.C.\underset{\displaystyle CH_3}{\underset{|}{C}}H.CH_2.CH_3 + C_6H_6 \xrightarrow{AlCl_3} C_4H_{10} + C_6H_5C(CH_3)_3$$

When 28.5 g of 2,2,3-trimethylpentane were reacted with 39 g of benzene in the presence of 3.33 g of aluminum chloride and 0.4 g of hydrogen chloride, 5.7 g of *tert*-butylbenzene and 11.5 g of isobutane were obtained That the total weight of the upper layer of the reaction mixture was 46.1 g indicates, however, that side-reactions predominate.

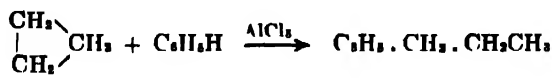
With the normal and simple isoparaffins, splitting may occur at various points along the chain, thus yielding C_3, C_4, C_5, and C_6 paraffins and the corresponding alkylated benzenes. This fact, coupled with such side-reactions as isomerization, intermolecular transfer of alkyl groups, and the disruptive effect of aluminum chloride on benzene itself, results in a great variety of reaction products. Reactions of *n*-pentane, isopentane, *n*-hexane, 2-methylpentane, and *n*-heptane with benzene were effected in sealed tubes at 125 to 175° for eight hours. With *n*-octane, *n*-decane, and hexadecane, maximum pressures of 10.5, 8, and 4.5 atmospheres were used, and reaction was effected at 125° for ten, twenty-three, and eight hours, respectively. 2,2,3-Trimethylpentane was reacted at ordinary pressure for eleven hours at 80-90°. It was indicated that conditions necessary for reaction of ethane, propane, or butane were so drastic that the benzene nucleus was disrupted.

Since 2,2,4-trimethylpentane reacts with benzene under mild conditions,[159] an investigation of its behavior with other aromatic hydrocarbons in presence of aluminum chloride and hydrogen chloride was made.[161] Reaction effected with toluene at ordinary pressure in presence of catalytic amounts of aluminum chloride on a water-bath for eight hours, during which time a continuous stream of dry hydrogen chloride was introduced into the reaction mixture, gave a 35 per cent yield of mono-*tert*-butyltoluenes, based on the paraffin reacting. With biphenyl, the reaction proceeded much more readily; here, too, a yield of approximately 35 per cent of mono-*p*-*tert*-butylbiphenyls was secured. Reaction with ethylbenzene and *p*-xylene was complicated by migration of the

[161] A. V. Grosse, J. M. Mavity, and V. N. Ipatieff, *J. Org. Chem.*, **3**, 448-455 (1938).

ethyl and methyl groups, yielding polyethyl and polymethylbenzenes. Fluorene condensed with itself to give bifluorenyl, but that the paraffin was involved in the reaction was shown by the fact that isobutane was a by-product. No alkylation occurred with either naphthalene or pyrene, the paraffin being recovered substantially unchanged.

Cycloparaffins react with aromatic hydrocarbons in the presence of aluminum chloride by primary cleavage of the cycloalkane ring and subsequent addition of the resulting chain to the aromatic hydrocarbon.[162] Ease of reaction, therefore, depends upon the comparative instability of the individual cycloparaffin. Since scission of the cyclopropane ring occurs readily, the reaction

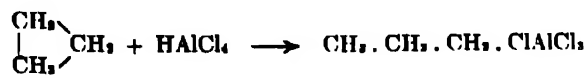


$$\begin{matrix} CH_2 \diagdown \\ | \quad\quad CH_2 \\ CH_2 \diagup \end{matrix} + C_6H_5H \xrightarrow{AlCl_3} C_6H_5 . CH_2 . CH_2CH_3$$

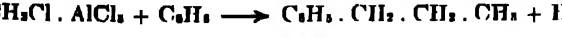
proceeds easily at temperatures of even below 0°. The only products are *n*-propylbenzene, and higher *n*-propylbenzenes formed by subsequent alkylation of the primary product. Isomerization of the alkyl group does not occur during reaction; the completely alkylated product was hexa-*n*-propylbenzene. From an experiment in which 42 g of cyclopropane was added to 175 g of benzene containing 8.75 g of aluminum chloride and 0.8 g of hydrogen chloride during five hours at +5° to 0°, the following products were isolated:

n-propylbenzene	74.3 g
dipropylbenzenes	11.1 g
higher liquid propylbenzenes	2.1 g
hexa-*n*-propylbenzene	4.0 g

The absence of isomerization in the reaction of cycloalkanes with benzene has been explained by the primary formation of difficultly isomerized alkylaluminum tetrachlorides from $HAlCl_4$, the addition product of aluminum chloride and hydrogen chloride[163]:



$$\begin{matrix} CH_2 \diagdown \\ | \quad\quad CH_2 \\ CH_2 \diagup \end{matrix} + HAlCl_4 \longrightarrow CH_3 . CH_2 . CH_2 . ClAlCl_3$$



$$CH_3 . CH_2 . CH_2Cl . AlCl_3 + C_6H_6 \longrightarrow C_6H_5 . CH_2 . CH_2 . CH_3 + HAlCl_4$$

Cyclopropane with *m*-xylene and aluminum chloride gives a 40 per cent yield of 1,3-dimethyl-4-*n*-propylbenzene. Here the entering alkyl group goes into the *p*-position, whereas in reactions with *n*- or isopropyl chloride, *m*-substitution is obtained.[164]

The reaction between methylcyclobutane and benzene with aluminum chloride and hydrogen chloride proceeds at 25°. Here the reaction products are more complex, for the scission of the cycloalkane ring may be

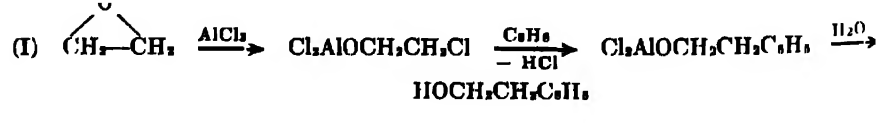
[162] A. V. Grosse and V. N. Ipatieff, *J. Org. Chem.*, 2, 447-458 (1937).
[163] V. N. Ipatieff, H. Pines, and L. Schmerling, *J. Org. Chem.*, 5, 253-263 (1940).
[164] D. Nightingale and B. Carton, *J. Am. Chem. Soc.*, 62, 280-3 (1940).

theoretically effected at four different places. Cyclopentane requires temperatures of about 150° in order to effect scission of the ring, and at this temperature isomerization and dealkylation occur. Some dehydrogenation of the cyclopentane takes place also, for one of the reaction products was found to be cyclopentylbenzene.[162]

The production of alkylated aromatic hydrocarbons by reaction of paraffins or cycloparaffins with aromatic hydrocarbons in the presence of aluminum chloride and hydrogen chloride has been covered by a number of patents assigned to Universal Oil Products Company.[165]

Addition of Alkylene Oxides to Aromatic Compounds

In 1925 it was reported by Schaarschmidt and co-workers[166] that, upon introducing two molecular equivalents of ethylene oxide, together with gaseous hydrogen chloride, into a mixture consisting of one equivalent of benzene and one equivalent of aluminum chloride at 10°, they secured a 1 per cent yield of β-phenylethyl alcohol and a 40 per cent yield of bibenzyl. Smith and Natelson[167] obtained a 5 per cent yield of the alcohol and a 65 per cent yield of bibenzyl by eliminating the use of hydrogen chloride and employing an excess of benzene instead of an excess of ethylene oxide. Under analogous conditions, bromobenzene gave 4,4′-dibromobibenzyl in 70 per cent yield; although no attempt was made to isolate the alcohol, its odor was noticed. The reaction appeared to be general for olefinic oxides and aromatic hydrocarbons or their derivatives, propylene oxide giving with benzene an 8 per cent yield of 1-phenyl-2-hydroxypropane and a 46 per cent yield of methylbibenzyl. According to Smith and Natelson, the course of the reaction proceeds through a primary addition of aluminum chloride to the olefinic oxide, and condensation of the resulting complex either with one molecule of the aromatic component to give the aralkyl alcohol or with two molecules of the aromatic compound to yield bibenzyl:



(I) $CH_2(O)CH_2 \xrightarrow{AlCl_3} Cl_2AlOCH_2CH_2Cl \xrightarrow[-HCl]{C_6H_6} Cl_2AlOCH_2CH_2C_6H_5 \xrightarrow{H_2O} HOCH_2CH_2C_6H_5$

(II) $CH_2(O)CH_2 \xrightarrow{AlCl_3} Cl_2AlOCH_2CH_2Cl \xrightarrow{2C_6H_6} C_6H_5.CH_2CH_2.C_6H_5$

The manufacture of alcohols from alkylene oxides and aromatic, alicyclic, or aliphatic hydrocarbons in presence of aluminum chloride was patented in 1931 by I. G. Farbenindustrie.[168] Since then a number of

[165] U. S. P. 2,068,598 (1937) and U. S. P. 2,104,424 (1937) to V. Ipatieff and A. V. Grosse (to Universal Oil Products Co.); Brit. P. 498,260 (1938) to Universal Oil Products Co.; *C. A.*, 33, 3809; French P. 830,037 (1938) to Universal Oil Products Co.

[166] A. Schaarschmidt, L. Hermann, and B. Saenzo, *Ber.*, 58, 1814-1816 (1925).

[167] R. A. Smith and S. Natelson, *J. Am. Chem. Soc.*, 53, 3476-3479 (1931).

[168] Brit. P. 354,992 (1931) to I. G., *Brit. Chem. Abs.*-B, 12 (1932); French P. 716,604 (1931) to I. G.; *C. A.*, 26, 2196; German P. 594,968 (1934) to I. G.; *C. A.*, 28, 5077; U. S. P. 2,029,618 (1936) to H. Hopff (to I. G.).

patents have been directed at improvement of the process. Dilution of the alkylene oxide with an inert gas and maintenance of the reaction temperature at 5-10°, and introduction of an aromatic or aliphatic amine with the alkylene oxide in order to neutralize the hydrogen chloride evolved have been claimed as advantageous.[169] According to another patent,[170] there is no definite minimum temperature necessary to produce recoverable quantities of phenylethyl alcohol, although it is stated that at 6° the formation of bibenzyl is practically negligible, and the yield of the alcohol amounts to 65 per cent of theoretical, based on the available ethylene oxide. Carpenter[171] specifies the use of at least 3.4 parts of aluminum chloride with 1 part of alkylene oxide. The rapid removal of the reaction product from the zone of reaction has been claimed to prevent formation of by-products.[172]

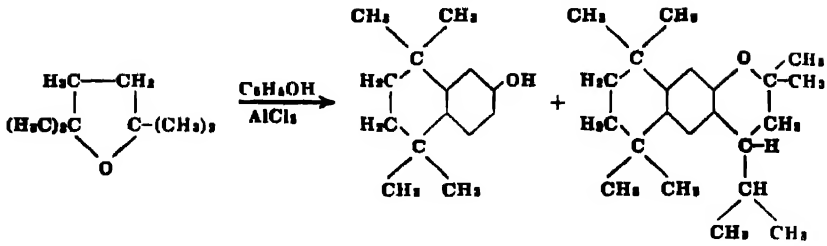
In a recent patent[173] the presence of a large excess of Friedel-Crafts reactant over the alkylene oxide and the aluminum chloride is stressed. Yields of phenylethyl alcohol secured by using a large excess of benzene are contrasted with yields obtained when a lower ratio of the hydrocarbon is used:

Benzene (lbs)	Ethylene Oxide (lbs)	Yield of Phenylethyl Alcohol (lbs)
1000	150	100
4000	150	160
6000	150	225

The excess of benzene serves to reduce polymerization of ethylene oxide; since there is present a large number of molecules of Friedel-Crafts reactant per molecule of alkylene oxide, Friedel-Crafts condensation is more likely to occur than self-condensation of the olefinic oxide. With costly materials, an added Friedel-Crafts reactant may serve as diluent and the mixture of two alcohols obtained may be subsequently separated. Examples of compounds which have been claimed as Friedel-Crafts reactants in this process include aromatic compounds such as benzene, toluene, cymene, naphthalene, chloro- or bromobenzene, anisole, phenetole, diphenyl ether, benzaldehyde, tolualdehyde, acetophenone and benzophenone, aliphatic compounds such as hexane, heptane and dodecane, cycloparaffins, or heterocyclic compounds such as pyridine, quinoline, or thiophene. The alkylene oxides include ethylene, trimethylene, propylene, and isobutylene oxides.

In the reaction of 2,2,5,5-tetramethyltetrahydrofuran with phenol and aluminum chloride, cycli-alkylation occurs, with production of 5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-2-naphthol:

[169] British P. 393,186 (1933) to L. Valik and I. Valik, *C. A.*, 28, 1047.
[170] Can. P. 340,555 (1934) to K. H. Klipstein (to E. C. Klipstein and Sons Co. to the Calco Chem. Co., Inc.); *C. A.*, 28, 4067.
[171] U. S. P. 2,012,710 (1935) to M. S. Carpenter (to Givaudan-Delawanna, Inc.); *C. A.*, 29, 6901.
[172] U. S. P. 2,125,490 (1938) to H. S. Davis (to Calco Chemical Co.); *C. A.*, 32, 7476.
[173] U. S. P. 2,125,908 (1938) to E. T. Theimer, *C. A.*, 32, 7476; *cf.* U. S. P. 2,047,896 (1936) to E. T. Theimer, *C. A.*, 30, 6005.



The chromane derivative, formed in lesser amounts, is produced by condensation of the naphthol derivative with an additional mole of the alkylating agent. Here, instead of addition as in the case of ethylene oxide, cyclodehydration occurs.[174]

Addition to the Cyanogen Group

According to Desgrez,[175] the action of cyanogen with benzene in presence of aluminum chloride results in simultaneous halogenation and formation of benzonitrile. Vorländer [176] had shown, however, that if cyanogen gas is passed during one hour into a mixture of 50 cc of benzene and 20 g of aluminum chloride, with cooling by water, 2 g of benzoyl cyanide is secured. Repeating the work of Desgrez resulted in production of benzoyl cyanide, together with a small amount of benzonitrile The amount of benzoyl cyanide in proportion to the nitrile obtained increased with decreasing temperature. The reaction was assumed to take place according to the scheme:

$$C_6H_6 + N \vdots C . C \vdots N \longrightarrow C_6H_5 . C(: NH) . CN$$

This intermediate was not isolated, but probably was responsible for the production of benzoyl cyanide upon hydrolysis of the reaction mixture

$$C_6H_5 . C(: NH) . CN + H_2O \longrightarrow C_6H_5COCN + NH_3$$

At higher temperatures the intermediate reaction product no doubt decomposes, with nitrile as final reaction product:

$$C_6H_5 . C . (: NH) . CN \longrightarrow C_6H_5 . CN + HCN$$

The intermediate formation of imine was substantiated by the fact that when the initial reaction mixture is allowed to stand for 48 hours before hydrolysis, the final product contains some benzil, and the amount of benzoyl cyanide is decreased:

$$C_6H_5 . C(: NH) . CN + C_6H_6 \longrightarrow C_6H_5 . C(: NH) . C(: NH) . C_6H_5$$

$$\xrightarrow{H_2O} C_6H_5 . CO . CO . C_6H_5$$

[174] H. A. Bruson and J. W Kroeger, *J. Am. Chem. Soc.*, 62, 38-44 (1940).
[175] A. Desgrez, *Bull. soc. chim.* (3), 13, 735-737 (1895); *J. Chem. Soc. Abs.*, 70 (I), 419 (1896) *Bc* , 29, *Ref.* 185 (1896); *C. Z.*, 1895, II, 998.
[176] D. Vorländer, *Ber.*, 44, 2456-2470 (1911); *C. A.*, 5, 3817.

From analogous reaction with toluene, effected by leading dicyanogen into a mixture of 100 g of toluene and 100 g of aluminum chloride at 40° for 6 hours, there were obtained 7.2 g of *p*-toluyl cyanide and 8 g of *p*-tolunitrile. When the reaction mixture was allowed to stand for 2 days, however, the product from 50 g of toluene and 50 g of aluminum chloride consisted of 2.5 g of *p*-tolunitrile, 1.7 g of *p*-toluic acid and 5.5 g of *p,p'*-dimethylbenzil. Heating the dicyanogen reaction mixture to 70° yielded 5 g of *p*-toluyl cyanide and 13.6 g of *p*-toluic acid. Reactions of dicyanogen with ethylbenzene, biphenyl, and phenetole were shown to proceed similarly.

The condensation of trichloroacetonitrile with aromatic hydrocarbons, phenols, or phenol ethers in the presence of aluminum chloride and hydrogen chloride affords a good method for the production of trichloromethyl-aryl ketones. The primarily formed ketimides are readily hydrolyzed to ketones:

$$Cl_3CC:N + HR \xrightarrow{AlCl_3} [R.C(:NH).CCl_3] \xrightarrow{H_2O} Cl_3C.CO.R + NH_3$$

The following compounds have been shown to undergo the reaction:

Aromatic Component	% Yield of $Cl_3C.CO.R$	Ref.
Benzene	70	1
Toluene	90	1, 4
o-Xylene	60	1
m-Xylene	94	1
p-Xylene	83	1
Mesitylene	73	1, 4
Naphthalene	29	1
Phenol	95	2, 4
o-Cresol	90	2
Thymol	73 (including ketimide)	4
m-Cresol	55 (mixt. of isomers)	2
p-Cresol methyl ether	71	2
1,3,4-Xylenol	70	4
Carvacrol	75 (including ketimide)	4
Diphenyl ether	70	3
2,3-Dimethylanisole	74	4
Tetralin	42 (of ketimide)	4
Thiophene	35	1
Chlorobenzene	poor yields	3
Chlorotoluenes	poor yields	3

References

1. J. Houben and W. Fischer, *J. prakt. Chem.*, 123, 313-329 (1929); *C. A.*, 24, 1106.
2. J. Houben and W. Fischer, *J. prakt. Chem.*, 123, 263-275 (1929); *C. A.*, 24, 91.
3. J. Houben and W. Fischer, *Ber.*, 64, 2645-2655 (1931); *Brit. Chem. Abs.-A*, 50 (1932).
4. J. Houben and W. Fischer, *Ber.*, 63, 2455-2462 (1930).

Chloroacetonitrile condenses with benzene in presence of aluminum chloride to give a product consisting of *o*-toluic acid, benzoic acid and *o*-tolunitrile, but only a small portion of the chloroacetonitrile takes part in the reaction.[177]

Reaction of aryl isothiocyanates and aromatic hydrocarbons occurs by addition of aryl at the double bond, with production of thioanilides

$$R\ N:CS + C_6H_6 \xrightarrow{AlCl_3} R.\overset{H}{\underset{|}{N}}.\overset{S}{\overset{\|}{C}}.C_6H_5$$

By the action of aluminum chloride on the isothiocyanate alone, a sulfide is simultaneously formed.[178] When phenol ethers are substituted for aromatic hydrocarbons, addition proceeds more readily; the rapid reaction rate prevents the formation of sulfides. Addition products of phenyl *o*-tolyl, *p*-tolyl, or *m*-xylyl isothiocyanates and anisole or phenetole were prepared.[179]

$$R.C_6H_4N:CS \xrightarrow[AlCl_3]{C_6H_5OR''} R.C_6H_4NHCSC_6H_4OR''$$

The thiobenzanilides secured are readily converted to thiobenzoic acid upon saponification[180]:

$$R.\overset{H}{\underset{|}{N}}.\overset{S}{\overset{\|}{C}}.C_6H_5 \xrightarrow{H_2O} RNH_2 + C_6H_5CSOH$$

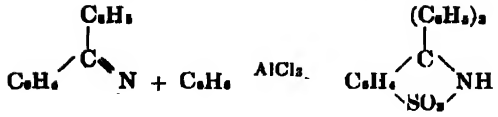
The reaction of phenyl isocyanate with benzene or benzene homologs in the presence of aluminum chloride has been postulated as occurring through intermediate formation of an arylcarbamyl chloride which then reacts with the benzene to form an anilide[181]:

$$C_6H_5CNO \xrightarrow[+\ HCl]{AlCl_3} ClCONHC_6H_5 \qquad C_6H_5CONHC_6H_5$$

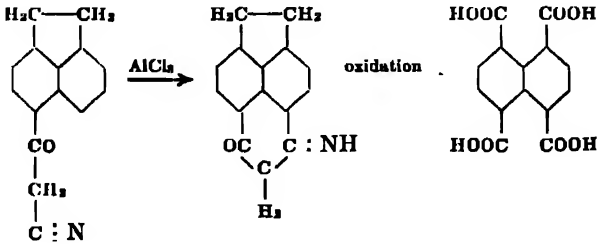
A mixture of cyanic acid and hydrogen chloride[182] or of alkali metal cyanate and hydrogen chloride[183] reacts analogously with aromatic hydrocarbons and aluminum chloride. Aromatic amides are secured

When 3-phenyl α,β-benzisothiazole is reacted with benzene and aluminum chloride addition occurs[184]:

[177] P. Genvresse, *Bull. soc. chim.*, 49, 579-581 (1888); *J. Chem Soc Abs*, 54, 951 (1888)
[178] A. Friedmann and L. Gattermann, *Ber.*, 25, 3525-3528 (1892).
[179] K. Tust and L. Gattermann, *Ber.* 25, 3528-3530 (1892)
[180] L. Gattermann, *J. prakt. Chem. (2)*, 59, 572-594 (1899); *J. Chem Soc Abs*, 76 (I), 694 (1899)
[181] R. Leuckart, *Ber.*, 18, 873-887 (1885); *J. Chem. Soc Abs*, 48, 773 (1885)
[182] L. Gattermann and A. Rossolymo, *Ber.*, 23, 1190-1199 (1890).
[183] German P. 554,143 (1933) to I. G.; *C. A.*, 26, 174.
[184] P. Fritsch, *Ber.*, 29, 2290-2301 (1896).



The conversion of 4-cyanoacetylacenaphthene to an imino- ketone which yields 1,4,5,8-naphthalenetetracarboxylic acid upon oxidation is catalyzed by aluminum chloride.[185]

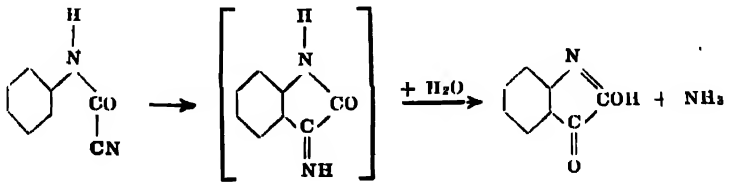


Similar products are obtained from 4- or 5-cyanoacetyl-3-chloroacenaphthene. The production of cyanoacetylacenaphthenes and their ring closure may be effected in one operation. Thus, the monoketimide of *peri*-acenaphthindandione is prepared in 50 per cent yield by condensing acenaphthene with cyanoacetyl chloride in the presence of aluminum chloride.[186]

Upon heating with a NaCl-$AlCl_3$ melt, isatin and its derivatives are secured from arylides of the general formula

$$\text{aryl} \cdot \dot{N} \cdot CO \cdot CN$$

in which the aryl substituent has a free ortho- position to the imino-group.[187] Isatin is secured from cyanoformanilide according to the scheme:

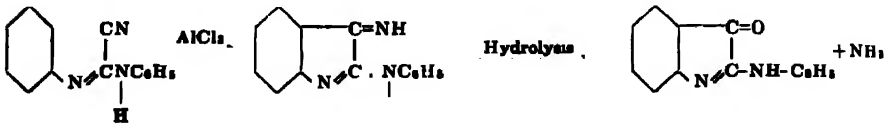


The reaction is likewise applicable to the preparation of naphthisatin, and to nuclear halogenated or alkylated derivatives of isatin or naphthisatin. N-Alkylcyanoformarylides yield N-substituted isatins upon

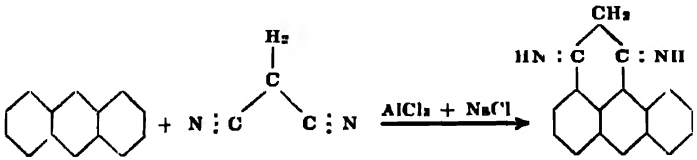
[185] British P. 342,879 (1929) to I. G.; *Brit. Chem. Abs.* B, 476 (1931); *C. A.*, 25, 5577.
[186] French P. 703,794 (1930) to I. G.; *C. A.*, 25, 4556. German P. 557,621 to I. G.; *C. Z.*, 1932, II, 2730.
[187] U. S. P. 1,792,170 (1931) to G. Kranzlein, A. Wolfrum and E. Hausdorfer (to General Anilin Works); German P. 541,324 to I. G.

treatment with aluminum chloride and hydrogen chloride in nitrobenzene.[188]

Hydrocyancarbodiphenylimides undergo ring closure to give isatin-α-arylides upon hydrolysis. Isatin-α-anilide is obtained as follows[189].



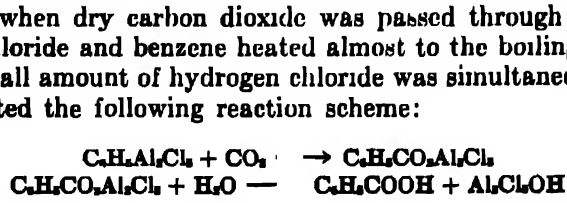
The dinitrile of malonic acid adds to aromatic hydrocarbons with formation of diketimides. With anthracene the diketimide of 1,9-anthracene indandione is formed:



Aromatic components, which may be substituted for anthracene in the foregoing reaction include toluene, naphthalene, acenaphthene, 1-methylnaphthalene and α- or β-naphthol ethers.[190]

Addition of Carbon Dioxide to Aromatic Compounds

Friedel and Crafts[191] observed that a small amount of benzoic acid was formed when dry carbon dioxide was passed through a mixture of aluminum chloride and benzene heated almost to the boiling point of the latter. A small amount of hydrogen chloride was simultaneously evolved They suggested the following reaction scheme:



$$C_6H_5Al_2Cl_5 + CO_2 \rightarrow C_6H_5CO_2Al_2Cl_5$$
$$C_6H_5CO_2Al_2Cl_5 + H_2O \rightarrow C_6H_5COOH + Al_2Cl_5OH$$

Pressures of 50-60 atmospheres at 80-150° may be used to prepare benzoic acid, *p*-chlorobenzoic acid, *p*-toluic acid, or 2,4-dimethylbenzoic acid from the corresponding hydrocarbons.[192]

Carbon dioxide in the presence of aluminum chloride reacts not only with hydrocarbons, but also with oxygenated derivatives. Thus, phenol and carbon dioxide in the presence of aluminum chloride may give 2,4′- or 4,4′-dihydroxybenzophenone, salicylic acid, aurin, or diphenyl ether by judicious variation of temperature and pressure, the latter derivative being formed at 200° under 120 atm pressure. Cresols yield products of

[188] German P. 515,542 to Deutsche Gold -und Silber-Scheideanstalt vorm Roessler
[189] German P 277,396 to Farbenfabriken vorm Friedr. Bayer & Co , *C. Z* , 1914, II, 675
[190] French P. 704,633 (1930) to I. G.; *C A* , 25, 4717; German P. 557,665 (1932) to I G , *C Z* 1932 II, 3623.
[191] C. Friedel and J M Crafts, *Compt rend* , 86, 1368-1371 (1878); *Ann chim. phys (6)*, 14, 433 472 (1888).
[192] Brit P. 307,223 (1928) to I. G.; *Brit. Chem. Abs* -B, 349 (1929) G. T. Morgan, *Chem and Ind* , 50, 104-109 (1931).

a similar type. Aniline forms diphenylurea, ethylaniline yields mainly monoethyldiphenylurea with some diphenylurea and *p,p'*-diethyldiaminobenzophenone, and dimethylaniline gives rise to the formation of tetramethyl-*p,p'*-diaminodiphenylmethane and *p*-dimethylaminobenzoic acid.[193]

Carbon suboxide reacts with benzene and aluminum chloride at 4° to give a small quantity of acetophenone, with benzoylacetic acid as an intermediate in the reaction.[194]

Addition of Sulfur Dioxide to Aromatic Compounds

Benzene sulfinic acid may be formed by the reaction of sulfur dioxide with benzene and aluminum chloride:

$$RH + SO_2 \longrightarrow RSO_2H$$

The reaction has been described by various workers.[195]

A complex, $AlCl_3.SO_2$ or $AlCl_2.SO_2Cl$, is formed which probably promotes condensation. Reaction is started by passing dry hydrogen chloride through the mixture. With this technic, the sulfinic acids of benzene, toluene, xylenes, mesitylene, cumene, cymene, naphthalene, chlorobenzene, and bromobenzene have been prepared. The free acids are unstable, but conversion to the sodium salt is a satisfactory method of preservation.

The reaction may also be applied to phenolic ethers,[196] but sulfoxides and sulfonium compounds are also produced. Anisole gives anisolesulfinic acid, di-*p*-anisyl sulfoxide, and trianisylsulfonium chloride. Phenetole reacts similarly. Smiles and Le Rossignol noted that the products of such reactions depend upon the nature and position of the groups already attached to the nucleus. Under certain conditions reaction proceeds to yield mainly any one of the three potential products. It has been noted, however, that *o*-cresyl methyl ether yields a sulfonium chloride and a sulfoxide.[197]

A reaction between fluorobenzene, hydrogen chloride, sulfur dioxide, and aluminum chloride in carbon disulfide as a solvent forms *p*-fluorobenzenesulfinic acid.[198]

Aluminum chloride is one of the catalysts which promote reaction between ethylene oxide, water, and hydrogen sulfide.[199] The nature of the products varies with the proportion of ethylene oxide used; thus, using molar amounts of water and hydrogen sulfide with 1, 2, or 3 moles of ethylene oxide the products were, respectively, thioethylene glycol, thiodiethylene glycol, and triethylolsulfinium hydroxide, the last being a strong base. The first reaction is quantitative, whereas that in which

[193] British P. 353,464 (1930) to G. T. Morgan and D. D. Pratt; G. T. Morgan, *loc. cit.*
[194] J. H. Billman, G. E. Tripp, and R. V. Cash, *J. Am. Chem. Soc.*, 62, 770-1 (1940).
[195] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2)*, 30, 1 (1878); *Compt. rend.*, 86, 1368-1371 (1878). G. Wagner, *Ber.*, 12, 852-858 (1879) E. Knoevenagel and J. Kenner, *Ber.*, 41, 3315-3322 (1908). G. E. Hilbert and T. B. Johnson, *J. Am. Chem. Soc.*, 51, 1526-1536 (1929); U. S. P. 1,903,063 (1933) to E. Havas (to E. I. du Pont); *C. A.*, 29, 2548.
[196] S. Smiles and R. Le Rossignol, *J. Chem. Soc.*, 93, 745-762 (1908); E. Knoevenagel and J. Kenner, *loc. cit.*
[197] G. B. Kohlatkar and K. V. Bokil, *J. Indian Chem. Soc.*, 7, 843-850 (1930); *Brit. Chem. Abs.-A*, (1931), 212.
[198] R. M. Hann, *J. Am. Chem. Soc.*, 57, 2166-2167 (1935)
[199] A. E. Chishibabin and M. A. Bestushev, *Compt. rend.*, 200, 242-244 (1935); *C. A.*, 29, 2509.

2 moles of ethylene oxide was used required cooling to prevent the formation of polyglycolic sulfides.

Many Friedel-Crafts reactions are carried out in the presence of carbon disulfide as a solvent, and small amounts of sulfur compounds are frequently obtained in the products.[200] These compounds appear to be carbithionic acids formed by the reaction:

$$RH + CS_2 \qquad RCS_2H$$

These acids may be decomposed during Friedel-Crafts reactions. In the presence of benzene, 5-10 per cent of neutral sulfur-containing resins were found to be formed. Phenetole forms a variety of products, some being alkali-soluble and probably of the type $ROC_6H_4CS_2H$ and $HOC_6H_4CS_2H$ and others, neutral products probably of the type $RSC_6H_4CS_2R$. The formation of ethyl *p*-hydroxydithiobenzoate was considered definite

Addition of Arsenous Oxide to Aromatic Compounds

Diarylaminohaloarsines may be prepared by treating arsenous oxide with a halogen salt of a diarylamine in the presence of aluminum chloride. Thus, diphenylaminechloroarsine is secured from diphenylamine hydrochloride and arsenous oxide.[201]

Addition of Dibenzoyl Peroxide to Aromatic Compounds

When dibenzoyl peroxide is reacted with benzene in the presence of aluminum chloride at 0°, phenyl benzoate and benzoic acid are formed almost quantitatively:

$$C_6H_5CO.O.O.OCC_6H_5 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COOC_6H_5 + C_6H_5COOH$$

An equimolar quantity of catalyst must be used for each mole of the peroxide transformed, since aluminum chloride forms a stable molecular complex with phenyl benzoate.[202] If reaction is not effected at low temperature, the reaction takes a different course, the products being benzoic acid, biphenyl, and carbon dioxide.[203]

Benzoyl peroxide reacts with chloroform at 0° according to the scheme[204]:

$$CHCl_3 + C_6H_5CO.O.O.OCC_6H_5 \xrightarrow{AlCl_3} C_6H_5COOH + C_6H_5COCl + COCl_2$$

[200] H. Jorg, *Ber.*, **60**, 1466-1470 (1927)
[201] U. S. P. 1,907,304 (1933) to W. Lofton, Jr., and S G Burroughs (to Pennsylvania Coal Products Co.); *C. A.*, **29**, 3690
[202] A. F. A Reynhart, *Rec trav chim.*, **46**, 54-61 (1927); *C. A.*, **21**, 1454. J. Boeseken and A F A Reynhart, *Verslag Akad Wetenschappen Amsterdam*, **29**, 598-602, *Brit. Chem. Abs.*-A, 1037 (1926), *ibid.*, **34**, 1099-1103 (1925); *C. A.*, **20**, 1998.
[203] H. Gilmsen and P H. Hermans, *Ber.*, **58**, 479-481 (1925), *C. A.*, **19**, 1858.
[204] A. F. A. Reynhart, *Rec trav. chim.*, **46**, 72-76 (1927); *Brit. Chem. Abs.*-A, 357 (1927)

Chapter 9

Addition Reactions. Part II

Synthesis of Keto-Acids from Dicarboxylic Acid Anhydrides

The addition of di- and polycarboxylic acid anhydrides to aromatic compounds in the presence of aluminum chloride is a widely used method for the preparation of keto-acids. Because the reaction has been extensively investigated, and because its course varies with the components involved, the following subdivisions will be used in the discussion which is given here:

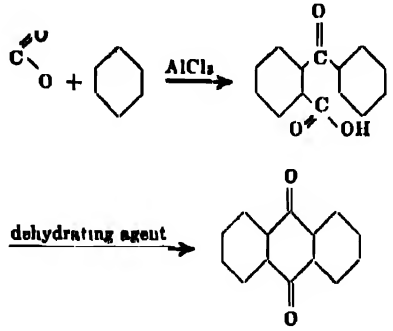
Aromatic di- and polycarboxylic acid anhydrides
- Phthalic anhydride
- Substituted phthalic anhydrides
- Other aromatic di- and polycarboxylic anhydrides

Heterocyclic di- and polycarboxylic anhydrides
Aliphatic di- and polycarboxylic anhydrides

Anhydrides of Aromatic Di- and Polycarboxylic Acids

The addition of dicarboxylic acid anhydrides to aromatic compounds is possibly the most commercially important of the reactions promoted by aluminum chloride. Both aromatic and aliphatic acid anhydrides react with aromatic hydrocarbons and a great many of their substitution products to yield a variety of keto-acids.

The basic reaction, and the one which has been most thoroughly investigated, involves the addition of benzene to phthalic anhydride to give *o*-benzoylbenzoic acid, which may be smoothly dehydrated to yield anthraquinone:



Inasmuch as anthraquinone and its derivatives are of fundamental importance to the dyestuffs industry, the keto-acids are valuable intermediates. Phthalic anhydride undergoes like reaction with

aromatic hydrocarbons other than benzene
halogenated hydrocarbons
phenols and phenol ethers
aromatic ketones and carboxylic acid derivatives
nitrogenous compounds
  nitro- compounds
  aryl amines
  amides
  ring compounds of nitrogen
sulfur compounds
  thioethers
  ring compounds of sulfur
oxygen ring compounds

The foregoing reactions, though resembling that of benzene with phthalic anhydride, necessarily involve differences in procedure and are, of course, subject to orienting and accelerating or retarding influences of the individual substituents. They are summarized in subsequent pages. Phthalic anhydride has also been found to add to aliphatic and hydroaromatic hydrocarbons. A discussion of this type of reaction is given in that section of this book which deals with the Friedel-Crafts reaction in aliphatic chemistry.*

Substituted phthalic anhydrides add to aromatic compounds substantially as does phthalic anhydride. Keto-acids have been obtained from the following derivatives of the anhydride:

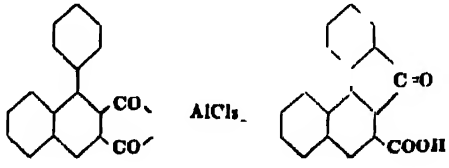
halogen	alkyl
nitro-	keto-
acetylamino-	sulfonyl
methoxy-	hydroxy-

A like reaction has been attempted with the anhydrides of other aromatic dicarboxylic acids. Although keto-acids are not formed in every case, reactions of aromatic compounds and aluminum chloride with the following dibasic acid anhydrides are discussed:

naphthalene dicarboxylic
biphenyl dicarboxylic
anthracene dicarboxylic
sulfobenzoic

Addition of tri- and tetracarboxylic acid anhydrides to aromatic compounds likewise does not necessarily result in the formation of keto-acids, nor does it always affect all carboxy- groups. Anhydrides of acids with the carboxy- groups in *o*-position generally add through these groups as does phthalic anhydride.

In some cases, anhydrides of dicarboxylic acids undergo ring closure instead of adding to benzene, with formation of cyclic ketones:



* See Chapter 17.

Reactions of this type may also occur with aryl-substituted aliphatic acid anhydrides in which a conveniently located phenyl group enables cyclization. They afford an efficient method for the preparation of compounds possessing carcinogenic activity.

Anhydrides of Heterocyclic and Alicyclic Dicarboxylic Acids

Similar reactions occur when heterocyclic dicarboxylic acid anhydrides react with aromatic compounds. Nitrogenous reactants of this type include quinolinic and cinchomeronic acid anhydrides. Sulfur compounds are represented by the dicarboxylic acid anhydrides of thiophene and thianaphthene. *o*-Dibasic lactonic acids also condense to yield keto-acids.

Alicyclic compounds such as the anhydrides of cyclopentane-1,1-diacetic acid and camphoric acid react with aromatic hydrocarbons in an analogous manner.

Aliphatic Dicarboxylic Acid Anhydrides

Condensations of the anhydrides of aliphatic dicarboxylic acids with aromatic compounds proceeds in the same manner as with phthalic anhydride. Thus maleic anhydride and benzene form β-benzoylacrylic acid, and succinic anhydride yields β-benzoylpropionic acid. Although most of the work in this field has been done with maleic and succinic anhydrides, considerable work has been done on the anhydrides of citraconic and other substituted maleic acids, pyrotartaric acid, phenyl- and other substituted glutaric acids, and adipic acid. These reactions are studied in the latter portion of this chapter.

PHTHALIC ANHYDRIDE AND AROMATIC HYDROCARBONS

Mechanism of the Reaction.—Investigations which have been made of the mechanism of the reaction have done much to clarify optimum conditions for the addition of phthalic anhydride to aromatic compounds. Friedel and Crafts [1] originally postulated that the reaction between toluene and phthalic anhydride occurs simply with the formation of the addition complex, $CH_3.C_6H_4.CO.C_6H_4.COO.Al_2Cl_5$, which yielded benzoic acid upon hydrolysis. Heller and Schülke,[2] however, suggested that the reaction proceeded through formation of an intermediate compound.

This view was not supported by Halla,[3] who found that, by reacting a mixture of benzene with toluene in varying proportions with phthalic anhydride and aluminum chloride, toluylbenzoic acid was secured almost exclusively. He concluded that toluene had reacted directly with phthalic anhydride and aluminum chloride and not on an intermediate compound. Addition of toluene after benzene, phthalic anhydride, and aluminum chloride had reacted gave no *o*-toluylbenzoic acid. Heller [4] pointed out that substitution of toluene occurred only upon addition to the intermediate compound, and not to the final complex.

[1] C. Friedel and J. M. Crafts, *Compt. rend.*, 92, 832-837 (1881); *J. Chem. Soc. Abs.*, 731 (1881).
[2] G. Heller and K. Schülke, *Ber.*, 41, 3627-3638 (1908).
[3] O. Halla, *Monatsh.*, 32, 637-640 (1911).
[4] G. Heller, *Ber.*, 45, 668-678 (1912).

Subsequently Rubidge and Qua,[5] McMullen,[6] and Lawrance and Oddy,[7] further characterized the intermediate complex by showing that in the presence of other anhydrides, *e.g.*, of acetic anhydride, it reacted with another mole of the hydrocarbon to give diaryl phthalides.

These investigations point to three conditions which influence the production of phthalide, thereby decreasing yields of keto-acids:

(1) Treatment of the primarily formed aluminum chloride complex with additional anhydride.

(2) Prolonged boiling of reaction mixture containing two or less molecular equivalents of catalyst (with respect to phthalic anhydride), and subsequent addition of more anhydride.

(3) Use of less than two moles of catalyst in the initial reaction mixture.

A 97 per cent yield of 2-benzoylbenzoic acid was obtained by Rubidge and Qua by adding phthalic anhydride to benzene, heating until the anhydride was dissolved, and then, after cooling, gradually adding 2 molecular equivalents of aluminum chloride (with respect to the phthalic anhydride). After standing for one hour at room temperature, the reaction mixture was boiled for two hours. Cooling was effected before decomposition of the catalyst complex with dilute hydrochloric acid. Variations from this procedure, either by using less than 2 moles of aluminum chloride at the beginning, or by adding more anhydride after boiling had continued for two hours, gave low yields of the keto-acid and high yields of the phthalide. If the reaction is initiated with only one mole of catalyst, and another mole of catalyst is not added until boiling has continued for two hours, diphenylphthalide is produced.

In a subsequent investigation of the reaction, McMullen [6] prepared a clear solution by adding at 10° two molecular equivalents of aluminum chloride to one molecular equivalent of phthalic anhydride in benzene. In the absence of the catalyst the anhydride is barely soluble in benzene at this temperature. Upon heating the clear solution with naphthalene for two hours, the product was found to consist of 60 per cent of benzoylbenzoic acid, 35 per cent of naphthoylbenzoic acid, and 5 per cent of naphthylphenylphthalide.

If, however, the clear solution is treated with an equal volume of anhydrous ether, and allowed to stand for thirty minutes, an oil is precipitated, which after washing with ether to free it from phthalic anhydride, gives only 2-benzoylbenzoic acid upon hydrolysis with dilute hydrochloric acid. If the oil is placed in a vacuum desiccator over sulfuric acid, it gives off benzene, ether, and hydrogen chloride and changes to a solid which seems to be identical with the final catalyst complex. Heating the oil on a water-bath for six hours with naphthalene dissolved in benzene yields no naphthoylbenzoic acid. An analysis of the oil showed

[5] C. R. Rubidge and N. C. Qua, *J. Am. Chem. Soc.*, 36, 732-737 (1914).
[6] T. C. McMullen, *J. Am. Chem. Soc.*, 43, 1955 (1921).
[7] W. A. Lawrance and H. G. Oddy, *J. Am. Chem. Soc.*, 44, 329-330 (1922).
[8] T. C. McMullen, *J. Am. Chem. Soc.*, 44, 2055-2060 (1922).

it to contain aluminum and chlorine in a ratio of 2:4.75, expressed in atomic weights.

The fact that the oil, or viscous precipitate, does not yield naphthoylbenzoic acid upon heating with naphthalene, whereas the clear solution does, indicates two definite stages in the reaction, which may be formulated as:

$$C_8H_4O_3 + C_6H_6 + Al_2Cl_6 \longrightarrow \text{clear solution} \longrightarrow \text{viscous precipitate} \longrightarrow \text{2-benzoylbenzoic acid}$$

McMullen carefully prepared the insoluble intermediate by shaking a mixture consisting of 5 g of phthalic anhydride, 9 g of aluminum chloride, and 80 cc of benzene for thirty minutes at room temperature, and boiling for two hours, at which time evolution of hydrogen chloride had ceased. When the content of the flask had been brought to constant weight it was analyzed and found to have the empirical formula $C_{14}H_9O_3Al_2Cl_5$. This intermediate compound was identical with the precipitate obtained by evaporation of the oil from the clear solution.

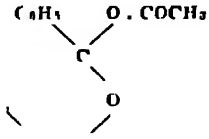
Although the insoluble intermediate compound represents the final reaction stage, treatment of it with toluene and acetic acid yields 0.14 g of benzoylbenzoic acid and 7.3 g of *p*-tolylphenylphthalide. An insoluble intermediate compound was then prepared from toluene in a manner analogous to that used for the preparation of the intermediate compound from benzene. Treatment of this complex with benzene and acetic acid yields nearly all 4'-methyl-2-benzoylbenzoic acid, and only 0.2 g of *p*-tolylphenylphthalide. The intermediate compound from benzene therefore reacts more readily with toluene than the intermediate compound from toluene reacts with benzene. In a similar experiment, reaction of the same amount of benzene intermediate with additional benzene yielded 2.5 g of diphenylphthalide.

Treatment of the insoluble intermediate from benzene with naphthalene and acetic anhydride and boiling for five hours gave a reaction product consisting of 5 parts by weight of 2-benzoylbenzoic acid, 3.5 parts of α-naphthylphenylphthalide, and 20 parts of β-naphthylphenylphthalide.

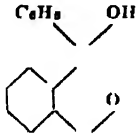
An insoluble intermediate compound was prepared from naphthalene, and then treated with benzene and acetic anhydride. Reaction indicated that the intermediate compound from benzene adds to naphthalene more readily than the intermediate compound from naphthalene reacts with benzene.

These experiments reveal that the final insoluble precipitate of phthalic anhydride keto- synthesis is incapable of reacting with hydrocarbons, but that it does react with hydrocarbons in the presence of added acetic anhydride. That the intermediate compound is not merely a phthalic anhydride-aluminum chloride complex has been shown by analysis of the complex from benzene; however, each complex exhibits properties peculiar to Friedel-Crafts reactive agents, that is, preferential condensation with the most aromatic, or active, component present.

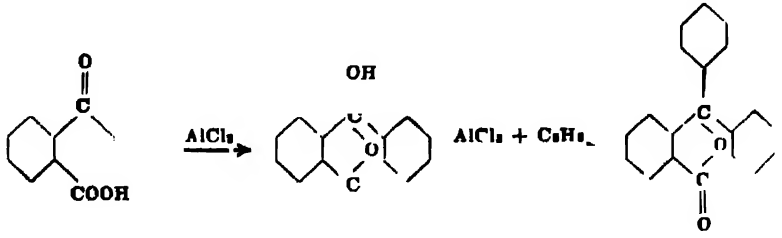
The effect of acetic anhydride on the reactivity of the insoluble intermediate parallels the observations made by von Pechmann in 1881.[9] This investigator prepared a mixed anhydride of 2-benzoylbenzoic acid and acetic acid by digesting one part of 2-benzoylbenzoic acid with two parts of acetic anhydride on a water-bath, and recrystallizing the reaction product from alcohol. On the basis of research dealing with esterification of keto-acids, Graebe [10] assigned the following structure to von Pechmann's mixed anhydride.



Graebe also assumed that in the presence of hydrochloric or sulfuric acid, 2-benzoylbenzoic acid reacted, during esterification, as hydroxylactone,



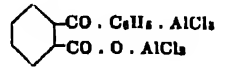
von Pechmann secured a theoretical yield of diphenylphthalide by heating his mixed anhydride with benzene in the presence of aluminum chloride until evolution of hydrogen chloride had ceased, but he was also able to secure diphenylphthalide by heating benzoylbenzoic acid with benzene in the presence of an excess of aluminum chloride, according to the scheme [11]:



In view of von Pechmann's work, the results of Rubidge and Qua and of McMullen point to the formation of a hydroxy- lactone of 2-benzoyl-

[9] H. F. von Pechmann, *Ber.*, 14, 1865-1867 (1881).
[10] C. Graebe, *Ber.*, 33, 3028-3033 (1900).
[11] *cf.* G. Kranzlein, "Aluminum chloride in der organischen chemie," p. 56, 1932.

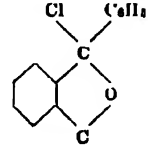
benzoic acid during reaction of the insoluble complex with acetic anhydride, and subsequent reaction of the esterified lactone with the most reactive hydrocarbon available to give the phthalide. Such an assumption involves possibly the following structure for the insoluble intermediate of benzene, $C_{14}H_8O_3.Al_2Cl_5$,



and a lactone structure for its esterification product.

That addition of benzoyl chloride to the reaction product of phthalic anhydride, benzene and aluminum chloride also results in the formation of diphenylphthalide in good yield [12] likewise bespeaks an intermediate which is sensitive toward esterifying agents in general.

Of interest is the fact that benzoylbenzoic acid has been assumed to form the lactone



upon treatment with phosphorus pentachloride. The product has been described as a brown, oily liquid; upon treatment with benzene and aluminum chloride it is converted to diphenylphthalide.[13]

The formation of diphenylphthalide if less than two molecular equivalents of aluminum chloride are used, or if heating is initiated rapidly,[14] may be explained by the fact that since the viscous complex is very readily attacked by anhydrides to yield diphenylphthalides, any unreacted phthalic anhydride in the reaction mixture will attack the complex and cause phthalide formation. It is therefore essential to provide material only in sufficient quantity to correspond to the complex $C_{14}H_8O_3.Al_2Cl_5$, and to insure homogeneous reaction by avoiding uneven heating. Use of temperatures above 50° likewise results in the formation of phthalides.

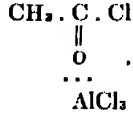
Phthalide production may also be explained by assuming that at least two moles of aluminum chloride and a reaction period of about two hours are necessary to effect fissure of the phthalic anhydride ring.

In reactions effected with anhydrides of monobasic acids, Groggins and Nagel [15] have found that 3 moles of aluminum chloride are required in order to secure at least partial utilization of the second carboxy- group.

[12] G. Haller, *Ber.*, 45, 665-673 (1912); *C. A.*, 6, 1439
[13] A. Haller and A. Guyot, *Compt. rend.*, 119, 139-142 (1894); *J. Chem. Soc. Abs.*, 66 (I), 801 (1894).
[14] P. H. Groggins, *Ind. Eng. Chem.*, 23, 153-160 (1931).
[15] P. H. Groggins and R. H. Nagel, *Ind. Eng. Chem.*, 26, 1313-1316 (1934).

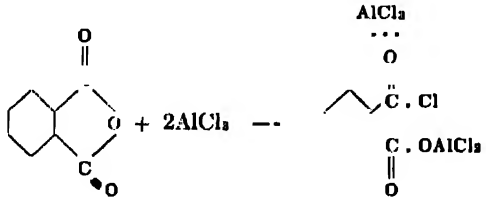
With acetic anhydride, the first mole of aluminum chloride splits up the anhydride, with formation of acetyl chloride and a complex:

The second mole of the catalyst is used to form a reactive complex with the acid halide $CH_3COCl.AlCl_3$. Unless a third mole of aluminum chloride is present, acylation is effected only with this complex. In the presence of a third mole of the catalyst, the complex $CH_3COOAlCl_2$ is converted into an acylating complex,

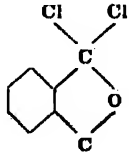


In the absence of a third mole of aluminum chloride, it is converted to acetic acid upon hydrolysis.

In view of these findings, the necessity of two moles of aluminum chloride for the production of keto-acids from phthalic anhydride may be explained by assuming a preliminary formation of a complex [16]:



In this connection it is of interest that in the reaction of phthaloyl chloride with benzene and aluminum chloride, rapid reaction leads to formation of diphenylphthalide, whereas the use of low temperatures with consequently longer reaction time induces the formation of 2-benzoylbenzoic acid.[17] Aluminum chloride causes conversion of phthaloyl chloride into its isomer,



[16] P. H. Groggins, "Unit processes in organic syntheses," p. 660, 1938.
[17] J. Scheiber, *Ann.*, **390**, 121-124 (1912).

A viscous, uncrystallizable, brown oil is first formed which, upon heating for forty hours, is changed into the crystalline aluminum chloride complex of the lactone.[18]

In spite of the vast amount of work which has been done on the reaction with phthalic anhydride, the composition of the primary product involved has not been clarified. Since solution of the anhydride in benzene upon treatment with aluminum chloride is effected with but little evolution of hydrogen chloride, McMullen's "clear solution" may well correspond to the phthalic anhydride-aluminum chloride complex assumed above. However, the fact that the clear solution yielded 60 per cent of benzoylbenzoic acid and only 35 per cent of naphthoylbenzoic acid upon boiling with naphthalene for two hours refutes this possibility, inasmuch as benzene is an efficient inert solvent for the preparation of 2-naphthoylbenzoic acid from naphthalene and phthalic anhydride in the presence of aluminum chloride.[19] McMullen does not give the amount of naphthalene added to the clear solution, but unless it were added only in minute quantity, the reaction would have given a preponderant amount of the naphthoylbenzoic acid if the clear solution were only a solution of a phthalic anhydride-aluminum chloride complex.

Factors Involved in Operation.—The preceding discussion of the mechanism indicates difficulties to be encountered in operation. Since formation of phthalides reduces the yield of keto-acids, conclusions derived from the study of phthalide formation made by Rubidge and Qua[20] are of interest in arriving at optimum conditions for the reaction:

(1) By employing 2 moles of aluminum chloride per mole of phthalic anhydride no phthalide is formed, and a yield of 97 per cent benzoylbenzoic acid is obtained. Similar results are obtained if more than 2 moles of aluminum chloride are used.
(2) Reducing the aluminum chloride to one mole cuts the keto-acid yield to less than 30 per cent, and a small amount of phthalide is formed; one-half mole of aluminum chloride gives very poor results. .
(3) Prolonged heating increase the phthalide formation.
(4) The addition of an extra mole of phthalic anhydride to the correct reaction mixture after reaction would normally be complete causes phthalide formation.
(5) The stepwise addition of aluminum chloride during reaction to reach the proper 2:1 ratio does not prevent phthalide formation.

To these chemical considerations Groggins[21] has added the following factors (developed from large-scale study) which promote phthalide formation:

(1) too rapid heating of the initial reaction mixture;
(2) inadequate mixing;
(3) an excessive reaction temperature.

[18] E. Ott, *Ann.*, 392, 274 (1912).
[19] German P. 193,901 (1907) to G. Heller. F. C. Whitmore and F. L. Carnahan, *J. Am. Chem. Soc.*, 51, 856-62 (1926). P. H. Groggins, *Ind. Eng. Chem.*, 23, 152-160 (1931)
[20] C. R. Rubidge and N. C. Qua, *J. Am. Chem. Soc.*, 36, 732-737 (1914).
[21] P. H. Groggins, *Ind. Eng. Chem.*, 23, 152-160 (1931)

Since keto-acids may be prepared in the presence of either a solvent or a diluent, a discussion of the procedure used necessarily falls into two categories.

Condensation with Solvents.—When diluents are used, the most economical procedure is to use an excess of the hydrocarbon if it is liquid at reacting temperatures, or is a solid of low melting point. With solid hydrocarbons earlier workers generally employed carbon disulfide. In 1908, however, Heller [22] claimed that excellent yields of naphthoylbenzoic or anthroylbenzoic acid are obtained by reaction of naphthalene or anthracene with phthalic anhydride and aluminum chloride if addition is effected in the presence of benzene, toluene, or xylene. The fact that, in the synthesis of keto-acids, reaction is effected with the most aromatic component present has already been mentioned in the discussion of the mechanism of the reaction.

In the preparation of 2-benzoylbenzoic acid, a mixture of phthalic anhydride and aluminum chloride is ground; benzene is introduced during the grinding, which is continued for several hours; the excess benzene is evaporated, and the resulting aluminum chloride compound of the keto-acid is obtained in dry, finely divided form [23]

A comparison of benzene, carbon disulfide, and *o*-dichlorobenzene as solvents in the condensation between phthalic anhydride, aluminum chloride, and naphthalene has been made by Groggins and Newton [24] The use of carbon disulfide does not give as high a yield of 2-(α-naphthoyl)-benzoic acid as that obtained by the use of benzene, or as pure a product as that obtained by the use of *o*-dichlorobenzene as solvent. The latter permits the use of lower solvent ratio and lower temperatures than with benzene, and yields a product of equal purity. Optimum yields of 2-(α-naphthoyl)benzoic acid were obtained by the action of 10 per cent excess aluminum chloride on molecular proportions of phthalic anhydride and naphthalene in 3-6 volumes of *o*-dichlorobenzene at 0-5°.

Halogenated benzenes react at high temperatures with phthalic anhydride and aluminum chloride, thus, at 100°, *o*-dichlorobenzene gives a 70 per cent yield of 3′,4′-dichloro-2-benzoylbenzoic acid [25] Although halogenated hydrocarbons react more slowly in the Friedel-Crafts reaction than does benzene or naphthalene, they cannot be used as solvents in reactions in which the components to be condensed are high-melting solids.

Nitrobenzene is more inert toward Friedel-Crafts reactions than are halogenated benzenes; however, it cannot be used as general solvent in the synthesis of keto-acids, since it has been shown to condense with tetrachlorophthalic anhydride and aluminum chloride to yield 2-(nitrobenzoyl)tetrachlorobenzoic acid [26]

Nitrobenzene has been found to be an especially efficient solvent in

[22] German P. 198,961 to G. Heller; *J. Chem. Soc. Abs.*, 94 (I), 648 (1908)
[23] Canadian P. 254,534 (1925) to H. G. Stone and B. H. Jacobson; *C. A.*, 20, 296.
[24] P. H. Groggins and H. P. Newton, *Ind. Eng. Chem.*, 22, 157-159 (1930).
[25] M. Phillips, *J. Am. Chem. Soc.*, 49, 473-478 (1927).
[26] A. Hoffmann, *Monatsh.*, 36, 805 (1915).

the acylation of phenols by reaction with acyl halides and aluminum chloride.* In the reaction with phthalic anhydride, the use of tetrachloroethane as solvent has been claimed to give uniformly good yields of 2-(hydroxybenzoyl)benzoic acids.[27] The condensation of *m*-cresol with 3-nitrophthalic anhydride, however, proceeds much better if a large excess of *m*-cresol is used instead of an indifferent solvent. Practically theoretical yields of the corresponding keto-acid are obtained.[28]

Tetrachloroethane has been shown to be an efficient solvent for reactions of polynuclear hydrocarbons or their derivatives with phthalic anhydride. α-Methoxynaphthalene thus gives a 91 per cent yield of 2-(4'-methoxynaphthoyl-1')-benzoic acid. The use of tetrachloroethane instead of nitrobenzene makes the method applicable to quantity production.[29] Tetrachloroethane has also given good results as solvent in the preparation of very pure 2-(α-naphthoyl)benzoic acid.[30] It has also been used as a solvent in the synthesis of keto-acid from chrysene,[31] and from tetralin.[32]

Temperature is an important factor in the preparation of keto-acids. According to Jacobson,[33] better yields and higher purity of product are obtained by carrying out the condensation of phthalic anhydride and an aromatic hydrocarbon (benzene or toluene) at temperautres of not more than 40-45°, and preferably at 25°.

Several patents have been directed at recovery of the keto-acid from the reaction mixture. Decomposition of the catalyst complex with cold dilute hydrochloric acid and filtration of the crystallized precipitate of acylbenzoic acid has been claimed.[34] Upon decomposition of the catalyst complex with 4 per cent hydrochloric acid, the keto-acid may be recovered by separation of the aluminum salt in a lower aqueous layer and the acyl benzoic acid in an upper layer of the excess solvent.[35] The use of low temperatures during hydrolysis of the catalyst complex, and recovery of the keto-acid as a salt have been claimed. The catalyst complex resulting from the treatment of an aromatic hydrocarbon and phthalic anhydride in the presence of aluminum chloride and large excess of solvent may be charged into ice and water at below 25°, and the aqueous aluminum salt solution removed by siphoning or decantation. The residual two layers are washed free from aluminum salts with water and are then made alkaline; the solvent is removed by steam distillation.[36]

* See p. 351.

[27] F. Ullmann and W. Schmidt, *Ber.*, 52, 2098-2118 (1919); *J. Chem. Soc. Abs.*, 116 (I), 53 (1920). A. M. v. d. Kneseback and F. Ullmann, *Ber.*, 55, 306-316 (1922); *J. Chem. Soc. Abs.*, 122 (I), 359 (1922).
[28] R. Eder and C. Widmer, *Helv. Chim. Acta*, 6, 419-424 (1923); *J. Chem. Soc. Abs.*, 124 (I), 988 (1923).
[29] L. F. Fieser and E. M. Dietz, *J. Am. Chem. Soc.*, 51, 3141-3148 (1929).
[30] M. Gallotti and P. Galimberti, *Ann. chim. applicata*, 22, 598-601 (1932); *C. A.*, 27, 288.
[31] Swiss P. 179,440 (1935) to Gesellschaft für chemische industrie in Basel; *C. Z.*, 1936, I, 2637.
[32] L. F. Fieser and R. N. Jones, *J. Am. Chem. Soc.*, 60, 1940-1945 (1938).
[33] U. S. P. 1,933,375 (1933) to B. H. Jacobson (to Calco Chemical Co.); *British Chem. Abs.*-B, 875 (1934).
[34] U. S. P. 1,942,490 (1934) to B. H. Jacobson (to Calco Chem. Co.); *Brit. Chem. Abs.*-B, 931 (1934).
[35] U. S. P. 1,547,250 (1925) to W. Wollaston; *C. A.*, 19, 2831 (1925).
[36] U. S. P. 1,718,569 (1929) to J. M. Tinker and I. Gubelmann (to New Port Co.); *Brit. Chem. Abs.*-B, 889 (1930).

Condensation without Solvents.—In condensations of aromatic hydrocarbons with phthalic anhydride, in the absence of a diluent, aluminum chloride need be used only in an amount which is approximately equimolecular to that of the components.[37] Such a procedure not only effects economy in the amount of catalyst required, but also obviates the following economic losses entailed by the use of solvent or an excess of the hydrocarbon [38]:

(1) cost of solvent recovery;
(2) loss of solvent or equivalent;
(3) increase in operating time;
(4) more complex and more costly operating system;
(5) additional problems regarding corrosion;
(6) deleterious effect on product.

Since thorough mixing and homogeneous heating are necessary, conducting the process without solvents has necessitated the use of especially efficient grinding and mixing equipment.

A charge consisting of 148 parts of phthalic anhydride, 266 parts of aluminum chloride, and 85 parts of benzene, when heated in a ball mill type of apparatus at 40-60°, during the addition of the benzene, and finally at 90-100°, yields 219 parts of 2-benzoylbenzoic acid, or 96 8 per cent of theoretical. Similarly toluene gave a 93.1 per cent yield of 4'-methyl-2-benzoylbenzoic acid, and chlorobenzene an 86 per cent yield of 4'-chloro-2-benzoylbenzoic acid when stirred in a ball mill.[37]

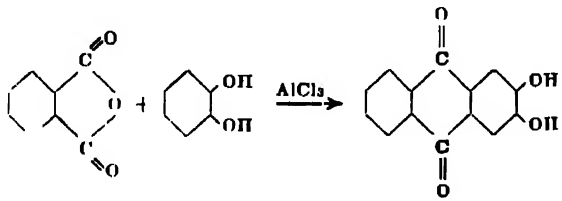
A ball mill for use in Friedel-Crafts synthesis of keto-acids has been described by Stone and Jackson.[39] Such a ball mill is mounted on a horizontal axis about which it revolves, and is partially filled with iron balls or blocks of various sizes which tumble about and effect the grinding of the charge as the mill rotates. The mill is equipped with a charging and a discharging vent, and an exit for the hydrogen chloride evolved It may be heated during reaction. The product becomes a viscous mass during the reaction, even when all the reactants are solid; and as the reaction progresses the viscous mass swells because of the evolution of hydrogen chloride gas. The aluminum chloride complex of the keto-acid is thus obtained directly as a fine, free-flowing powder which can be run out and decomposed in another vessel to form the keto-acid. The apparatus and the procedure have been thoroughly described by Groggins.[40]

The method has been used by Groggins [41] in the preparation of keto-acids from biphenyl or its chloro- derivatives. 4'-Phenyl-2-benzoylbenzoic acid is obtained, in yields amounting to about 95 per cent of theoretical, when a mixture of 1 mole of biphenyl, 1 mole of phthalic anhydride, and 2.2 moles of aluminum chloride is heated at 60-65° in a horizontal iron mill partially filled with loose iron blocks.

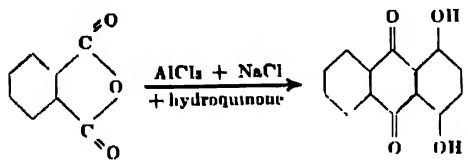
[37] German P. 495,447 (1927) to W. Muller (to I G); *C. A* , 24, 3251 (1930).
[38] P. H. Groggins, *Ind Eng. Chem.*, 23, 152-160 (1931)
[39] U. S. P. 1,656,575 (1928) to H G Stone and B H Jackson; *C. A.*, 22, 966.
[40] P. H. Groggins, *loc cit* ; "Unit Processes in Organic Syntheses," pp 668-675, 1938.
[41] P. H. Groggins, *Ind. Eng. Chem.*, 22, 620-630 (1930).

The effect of temperature in the production of 2-benzoylbenzoic acid by this method has been studied by Gallotti and Beretta.[42] By intimately mixing in a ball mill the stoichiometric proportions of phthalic anhydride, benzene and aluminum chloride, and heating for twenty hours at 50-60°, a 93.6 per cent yield of the keto-acid was obtained, whereas heating for twelve hours at 60-65° gave a yield of 96.1 per cent.

One-Step Production of Quinones.—The preparation of a keto-acid and its conversion into anthraquinone may be performed in one step if the reaction is conducted at high temperatures or in the presence of an $AlCl_3$-NaCl melt. At high temperatures, in the presence of aluminum chloride, condensation of phenols with phthalic anhydride yields hydroxyanthraquinones directly, without isolation of the keto-acids.[43] It is advantageous to use an excess of phthalic anhydride, which acts as a solvent when the reaction is effected at 180-250°. In this way pyrocatechol yields hystazarin, directly [44]:



Instead of using excess phthalic anhydride as diluent, sodium chloride may be used with the catalyst. Introduction of a phenol, like pyrocatechol, and phthalic anhydride heated to 110°, into a fused mass of aluminum chloride and sodium chloride yields the hydroxy- keto-acid;[45] however, at temperatures of approximately 200°, quinones are secured. In this way hydroquinone yields quinizarin [46]:



Haloquinizarins may be obtained by adding a halogenated phthalic anhydride and hydroquinone to an $AlCl_3$-NaCl melt and then maintaining a temperature of 200-220° for about twenty minutes. In this way an 84 per cent yield of 5,8-dichloroquinizarin is obtained.[47]

[42] M. Gallotti and A. Beretta, *Ann. chim. applicata*, 22, 691-694 (1932); *C. A.*, 27, 1629.
[43] German P. 282,493 and 292,066 to F. Ullmann.
[44] German P. 298,345 (1916) to Farbenfabriken vorm Friedr. Bayer & Co.; *C. Z.*, 1917, II, 256.
[45] German P. 642,719 (1937) to H. Waldmann (to I. G.); *C. A.*, 31, 6261; *cf.* H. Waldmann and P. Sellner, *J. prakt. Chem.*, 150, 145-153 (1938); *C. A.*, 32, 4573.
[46] H. Raudnitz, *Ber.*, 62, 509-513 (1929).
[47] H. Waldmann and H. Mathiowetz, *J. prakt. Chem. (2)*, 126, 250-256 (1930); *C. A.*, 24, 4294. H. Waldmann and H. Hartisch, *J. prakt. Chem. (2)*, 130, 92-102 (1931); *Brit. Chem. Abs.-A*, 846 (1931).

Table 23.

Hydrocarbon	m p of Derivatives (°C)	Ref.
Toluene	137–138	1–7, 11
o-Xylene	162	8, 9
m-Xylene		6
p-Xylene	149	10
Mesitylene	211–212	1
Pseudocumene		11
Durene (1,2,4,5-tetramethylbenzene)	263–265	1, 11
Ethylbenzene	122	12
m-Diethylbenzene	114–116	1
sym-Triethylbenzene	129.5–130.5	1
n-Propylbenzene	125–126	1, 12
Cumene (isopropylbenzene)	133–134	1
m-Diisopropylbenzene		13
Cymene	123–124	1, 6, 14
n-Butylbenzene	97–98	1
sec-Amylbenzene		15
Hexylbenzene		15
Heptylbenzene		15
Octylbenzene		15
Biphenyl	224–225	1, 16–19
Tetramethylbiphenyl		20
o,o'-Bitolyl	95–100	46
p,p'-Bitolyl	177–179	46
Naphthalene	172–173	1, 8, 21–26
1-Methylnaphthalene	167–169	27
2-Methylnaphthalene	190–191	27
Tetralin	153–155	1
6-Methyltetralin	167.5–168	48
m-Diphenylbenzene		49
Fluorene	227–229	1, 28, 29
Acenaphthene	198–200	1, 43–45
Anthracene	242–243	23, 30, 2
Phenanthrene	115	30, 41, 42
sym-Octahydrophenanthrene		40
Fluoranthene	212–214	2, 31, 36, 50
Pyrene	225–226	32, 33, 37, 38
Chrysene	210–213	34, 47
Hydrindene		39
Perylene		35

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13. O. R. Quayle and E. E. Reid, *J. Am. Chem. Soc.*, 47, 2357-2361 (1925).
14. M. Phillips, *J. Am. Chem. Soc.*, 46, 2535-2536 (1924)
15. H. A. Bruson, U. S. P. 1,934,033 (to Resinous Products and Chem. Co., Inc.); also U. S. P. 1,932,520-1.
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Table 23—*Continued*

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36. J. von Braun, G. Manz, and B. Kratz, *Ann.*, 496, 170-196 (1932).
37. J. W. Cook, C. L. Hewett, and I. Hieger, *J. Chem. Soc.*, 395-405 (1933).
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45. O. B. May, U. S. P. 1,997,305 (1935).
46. R. Scholl and C. Seer, *Ber.*, 44, 1091-1103 (1911).
47. German P. 652,912 (1937) to H. Vollmann and H. Becker (to I. G.); *C. Z.*, 1938, I, 2065.
48. L. F. Fieser and R. N. Jones, *J. Am. Chem. Soc.*, 60, 1940-1945 (1938).
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The method of preparing quinones by fusion of aromatic dicarboxylic acid anhydrides and a reactive substance with an $AlCl_3$-NaCl melt has been used for the preparation of vat dyes from phthalic anhydride and pyrenemonophthaloylic acid,[48] from phthalic anhydride and rubicene,[49] or from perylene.[50] Treatment of dibenzanthrones and carboxylic acid anhydrides with $AlCl_3+SbCl_3$ likewise yields vat dyes.[51]

Condensation of Phthalic Anhydride with Aromatic Hydrocarbons other than Benzene

Alkylated benzenes and polynuclear hydrocarbons add to phthalic anhydride even more readily than does benzene. It has been suggested that the isolation of the keto-acids formed would serve as a ready means of identifying the aromatic hydrocarbons present in a mixture.[52] Data concerning the melting points, theoretical and actual neutralization equivalents, and the conditions for crystallization of acids from 19 hydrocarbons are presented.

A critical examination has been made by Oliverio [53] of literature pertaining to constitution of benzoylbenzoic acid derivatives, especially with reference to orientation of the methyl and hydroxy- groups.

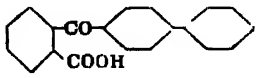
Preparations of keto-acids by addition of phthalic anhydride to an aromatic hydrocarbon in the presence of aluminum chloride are listed in Table 23.

The condensation of some of the alkylated benzenes with phthalic

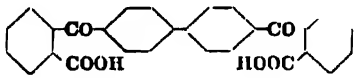
[48] Brit. P. 469,833 (1936) to Soc. chem. Ind. in Basle; *Brit. Chem. Abs.*-B, 1184 (1937).
[49] German P. 636,554 (1938) to H. Greune and G. Langbein (to I. G.); *C. A.*, 32, 4351.
[50] German P. 642,650 (1937) to P. Nawiasky and O. Grosskinsky (to I. G.); *C. A.*, 31, 6475.
[51] U. S. P. 2,058,477 (1936) to W. H. Lycan (to du Pont); *Brit. Chem. Abs.*-B, 1183 (1937); U. S. P. 2,058,606-7 (1936) to W. H. Lycan (to du Pont); *Brit. Chem., Abs.*-B, 1183 (1937).
[52] H. W. Underwood, *J. Am. Chem. Soc.*, 57, 940-942 (1935); *C. A.*, 29, 4351.
[53] A. Oliverio, *Gazz. chim. ital.*, 62, 231-243 (1932); *C. A.*, 26, 4324.

anhydride forms resinous masses rather than crystalline acids.[54] Bruson attributes this tendency to the probable formation of isomers, and noted that the increase in the length of the alkyl side chain from butylbenzene to octylbenzene increased the formation of resinous products.

The influence of the presence or absence of a solvent may be of importance in directing the course of the reaction. Aluminum chloride promotes the condensation of biphenyl and phthalic anhydride in carbon disulfide solution to form only 4'-phenyl-2-benzoylbenzoic acid:

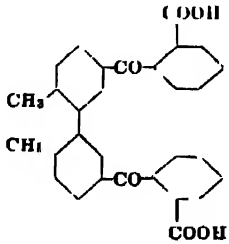


but if reaction is effected by heating to 100°C, in the absence of a solvent, the products are 2-phenylanthraquinone, 4,4'-bis(2"-carboxybenzoyl)-biphenyl,



and 4'-(3"-anthraquinonyl)-2-benzoylbenzoic acid with only a small amount of 4'-phenyl-2-benzoylbenzoic acid.[55] It has also been observed, however, that by holding the reaction temperature at 60-65°C and keeping the reactants thoroughly mixed in a horizontal rotating mill, a yield of 95 per cent of 4'-phenyl-2-benzoylbenzoic acid can be obtained from 1 mole of biphenyl, 1 mole of phthalic anhydride, and 2.2 moles of aluminum chloride.[56]

o,o'-Bitolyl yields the dibasic acid,[57]



and 2,4,2',4'-tetramethylbiphenyl[58] as well as pyrene[59] yield dicarboxylic products when reacted with phthalic anhydride and aluminum chloride.

Halogenated Hydrocarbons and Phthalic Anhydride

The presence of halogen in the benzene nucleus has a retarding effect on reaction with phthalic anhydride, so that higher temperatures are

[54] H. A. Bruson, U. S. P. 1,933,520-1, 1,934,033 to Resinous Products and Chemical Co., Inc. O. R. Quayle and E. E. Reid, *J. Am. Chem. Soc.*, 47, 2357-2361 (1925).
[55] R. Scholl and W. Neovius, *Ber.*, 44, 1075-1090 (1911).
[56] P. H. Groggins, *Ind. Eng. Chem.*, 22, 620-630 (1930); U. S. P. 1,814,145 (1931).
[57] R. Scholl and C. Seer, *Ber.*, 44, 1091-1108 (1911).
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[59] Swiss P. 160,427 (1930) to Soc. pour l'ind. chim. a Bale; *C. A.*, 32, 800.

necessary to effect addition. With chlorobenzene, temperatures of at least 50° generally are used, but with *o*-dichlorobenzene, reaction is best effected at 100°. The reaction has been effected with bromo-, iodo-, and fluoro- derivatives of benzene, but yields are poorer because of decomposition of the halogenated hydrocarbon by the catalyst.

The production of 4′-chloro-2-benzoylbenzoic acid from chlorobenzene and phthalic anhydride has been reported by numerous investigators to proceed smoothly.[60]

Condensation may be effected at 50-90° to give good conversion.[61] At temperatures of 80-100°, equimolecular proportions of phthalic anhydride, mono-halobenzene, and aluminum chloride may be used.[62] 4′-Chloro-2-benzoylbenzoic acid, obtained in 94 per cent yield by Friedel-Crafts reaction of phthalic anhydride and chlorobenzene, is an intermediate in the preparation of alizarin.[63]

4′-Bromo-2-benzoylbenzoic acid has been reported to be the product obtained by Friedel-Crafts reaction of bromobenzene with phthalic anhydride.[64] However, the decomposing action of aluminum chloride on bromobenzene has been especially noted by Prosser [65] who was unable to secure conversion to the halogenated keto-acid. Using the calculated amount of bromobenzene, or an excess, he was able to secure only 2-benzoylbenzoic acid.

Groggins and co-workers, on the other hand, have been able to secure an 80-85 per cent yield of the 4′-bromo derivative.[66] The reaction was studied in the liquid phase, using an excess of bromobenzene as diluent at 60-90°, as well as in an iron mill apparatus, using approximately molecular equivalents of bromobenzene and phthalic anhydride at 70-80°. In both processes 2.2 moles of aluminum chloride was used. Recovery of the excess bromobenzene used in the liquid phase reaction was only 90-93 per cent of the calculated amount, but yields of the keto-acid were slightly better, indicating decomposition of the bromobenzene. The fact that yields in excess of 80 per cent of the keto-acid showed that the reaction leading to cleavage of bromine was slower than that leading to formation of keto-acid.

Iodobenzene is also decomposed by aluminum chloride and gives only a small yield of 4′-iodo-2-benzoylbenzoic acid, together with iodine and

[illegible] Groggins and

1,699,671 (1929) to W. Müller and E. Appenzeller [illegible] (1929) to J. M. Tinker and I. Gubelmann; U. S. P. 1,746,736 (1930) to W. M. [illegible] Aniline & Chem. Co.); German P. 75,288 (1894) to G. Heller; German P. 495,447 (1927) *C. A.*, 24, 3251.

[61] U. S. 1,746,736, *loc. cit.*

[62] U. S. 1,699,671, *loc. cit.*

[63] P. P. Karpukhin, *loc. cit.*

[64] G. Dougherty and A. H. Gleason, *loc. cit.* F. Ullmann and M. Sone, *Ann.*, 380, 336-341 (1911); G. Heller, *Ber.*, 45, 665-673 (1912).

[65] R. A. Prosser, *Proc. Trans. Roy Soc. Can (3)*, 18, Sec III, 118-119 (1924); *C. Z.*, 1925, I, 1491

[66] P. H. Groggins, A. J. Stirton, and H. P. Newton, *Ind. Eng. Chem.*, 23, 893-899 (1931); *C. A.* 25, 4877.

some 2-benzoylbenzoic acid.[67] Fluorobenzene, however, condenses readily, to give a good yield of 4'-fluoro-2-benzoylbenzoic acid.

o-Dichlorobenzene is less reactive in the Friedel-Crafts reaction than is the monohalogenated derivative. At 50° it does not condense with phthalic anhydride. At 65° condensation to the extent of 5 per cent is effected, but only upon continued heating.[68] At 100°, it reacts to give an approximately 70 per cent yield of 3',4'-dichloro-2-benzoylbenzoic acid;[69] but at 175° the yield is only 20 per cent, because of formation of 2,3-dichloroanthraquinone.[70]

Table 24.

Halogenated Alkyl Benzene	Product: -2-benzoylbenzoic acid	Ref
o-Chlorotoluene	2'-chloro-3'-methyl- 4'-chloro-3'-methyl-	1, 2, 3
m-Chlorotoluene	4'-chloro-2'-methyl- 2'-chloro-4'-methyl-	4, 5
p-Chlorotoluene	2'- or 5'-methyl-5'- or 2'-chloro-	2, 6, 7
o-Fluorotoluene	3'-fluoro-4'-methyl-	8
m-Fluorotoluene	2'-fluoro-4'-methyl-	4
p-Fluorotoluene	5'-fluoro-2'-methyl- 2'-fluoro-5'-methyl-	8
o-Bromotoluene		9, 10
m-Bromotoluene	3'-methyl-4'-bromo-	4, 9, 10
p-Bromotoluene		9, 10
p-Iodotoluene	no iodo-acid	4
4-Fluoro-*m*-xylene	3'-fluoro-2',6'-dimethyl-	8
o-Chloroethylbenzene	3'-chloro-4'-ethyl-	4
o-Fluoroethylbenzene	3'-fluoro-4'-ethyl-	4
p-Fluoroethylbenzene	2'-ethyl-5'-fluoro-	4

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9. G. Heller and K. Müller-Dardoff, *Ber.*, 58, 497-499 (1925).
10. G. Heller, *Ber.*, 45, 792-796 (1912); *C. A.*, 6, 1617.

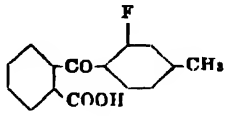
Condensation of *m*-dichlorobenzene with phthalic anhydride and aluminum chloride has been claimed to yield 2',4'-dichloro-2-benzoylbenzoic acid.[71] 2',5'-dichloro-2-benzoylbenzoic acid has been prepared by heating 1 mole of phthalic anhydride with 0.5 mole of *p*-dichlorobenzene, and 1.5 moles of aluminum chloride at 110-120° for about four hours.[72] A better yield (59.3 per cent) is obtained by heating 1 mole of the anhydride

[67] F. C. Hahn and E. E. Reid, *J. Am. Chem. Soc.*, 46, 1645-1653 (1924).
[68] P. H. Groggins and H. P. Newton, *Ind. Eng. Chem.*, 22, 157-159 (1930).
[69] M. Phillips, *J. Am. Chem. Soc.*, 49, 475-478 (1927).
[70] M. Tanaka and N. Tanaka, *Bull. Chem. Soc. Japan*, 3, 285-287 (1928); *C. A.*, 23, 1408. *cf.* H. E. Fiers-David, *J. Am. Chem. Soc.*, 49, 2334 (1927).
[71] British P. 268,884 (1927); U. S. P. 1,711,144 (1929) to I. Gubelmann, H. J. Wieland, and O. Stallmann; *Brit. Chem. Abs.*-B, 440 (1928).
[72] M. Phillips, *J. Am. Chem. Soc.*, 48, 3196-3199 (1926); *cf.* G. Dougherty and A. H. Gleason, *J. Am. Chem. Soc.*, 52, 1024-1027 (1930).

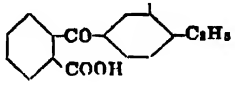
with 5 moles of the dichlorobenzene and 4 moles of aluminum chloride at 110° for six hours.[73]

Reported condensations of halogenated alkyl benzenes with phthalic anhydride and aluminum chloride are listed in Table 24.

The reaction with bromotoluene is noteworthy inasmuch as the same compound, 3'-methyl-4'-bromo-2-benzoylbenzoic acid, is obtained from *o*-, *m*-, or *p*-bromotoluene in 75 per cent yield. In the case of *m*-fluorotoluene, condensation may occur *para*- either to the methyl or to the fluorine. The results indicated the formation of isomers, but since the influence of the methyl group is stronger than that of fluorine it was concluded that the bulk of the product was



The corresponding acids from *m*-chloro- and *m*-bromotoluene could not be obtained in a pure state. *o*-Fluoroethylbenzene may condense with phthalic anhydride to yield four isomeric acids but the main product was found to be



and *o*-chloroethylbenzene gave a similar acid. Iodotoluene evolved iodine when the condensation reaction was attempted, probably because of the influence of the methyl group, although this observation is in accord with the results obtained in trying to condense iodobenzene with phthalic anhydride.

In the condensation of mono-chlorinated biphenyls with phthalic anhydride, the relative position of the halogen is unaltered. From 2- or 4-chlorobiphenyl, the products are 2''- or 4''-chloro-4'-phenyl-2-benzoylbenzoic acids. A 93.4 per cent yield of the 4''-chloro- keto-acid was obtained by heating the reactants at 65-70° for fourteen hours in an iron mill. Slightly lower yields were secured with 2-chlorobiphenyl; heating at 65-70° for fifteen hours gave an 84.1 per cent yield. In both cases 1 mole of the chlorobiphenyl, 1 mole of phthalic anhydride, and 2.2 moles of aluminum chloride were used.[74]

α- and β-Chloronaphthalene have been shown to undergo normal condensation, with production of the corresponding keto-acids;[75] but 1,4-dichloronaphthalene condenses to give a mixture of acids.[76] 2-Chloro-

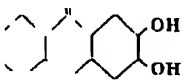
[73] I. M. Kogan and T. N. Ganina, *Org. Chem. Ind. (U. S. S. R.)*, 1, 87-91 (1936); *C. A.*, 30, 5216.
[74] P. H. Groggins, *Ind. Eng. Chem.*, 22, 620-630 (1930).
[75] G. Heller, *Ber.*, 45, 665-673 (1912).
[76] H. Waldmann, *J. prakt. Chem. (2)*, 131, 71-81 (1931).

1-methylnaphthalene, however, reacts to give 6'-chloro-2'-methyl-2-α-naphthoylbenzoic acid.[77]

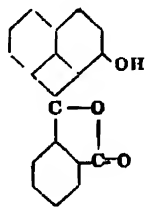
Condensation with Phenols and Phenol Ethers

The application of Friedel-Crafts synthesis of aromatic keto-acids has been extended to the condensation of phthalic anhydride and aluminum chloride with phenols, naphthols, hydroxyanthracenes, and their ethers In these reactions, the carbonyl group usually attaches itself to the carbon atom in *ortho-* position to the hydroxy- or ether group. Carbon disulfide and tetrachloroethane are usually used as solvents, but some reactions have been found to proceed more satisfactorily without solvent

Fusion at 180-250° with an excess of phthalic anhydride serving as diluent leads to formation of hydroxyanthraquinones.[78] Pyrocatechol thus gives hystazarin,

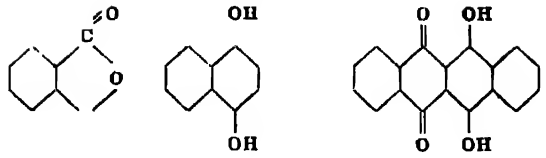


without isolation of the keto-acid intermediately formed. Although the method has been claimed to be general for hydroxyaromatics, Fieser [79] was unable to obtain a hydroxynaphthanthraquinone from β-naphthol, instead, a yellow compound having the composition $C_{18}H_{10}O_3$ of the following probable structure was obtained:

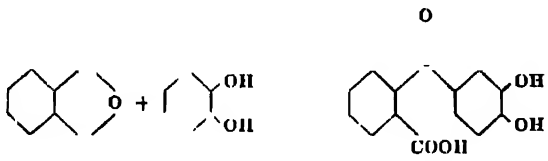


Ring closure without isolation of the intermediately formed keto-acids may also be achieved by fusion at about 200° with an $AlCl_3$-NaCl melt. Thus introduction of 30 g of 1,4-dihydroxynaphthalene and 28 g of phthalic anhydride into an $AlCl_3$-NaCl melt (235 g:47 g) at 200° and heating for one hour at 230-240° results in the production of 1,4-dihydroxy-2,3-benzanthraquinone [80]:

[77] R. Scholl, C. Seer, and A. Zinke, *Monatsh.*, 41, 553-602 (1921); *J. Chem. Soc. Abs.*, 120, 677 (1921).
[78] German P. 298,345 (1917) to Farbenfabriken vorm Friedr. Bayer & Co.; *C. Z.*, 1917, II, 256
[79] L. F. Fieser, *J. Am. Chem. Soc.*, 53, 3546-3560 (1931).
[80] H. Raudnitz, *Ber.*, 62, 509-513 (1929).



At lower temperatures the use of an $AlCl_3$-NaCl melt results only in the production of the keto-acids. The addition of 66 g of phthalic anhydride and 44 g of *o*-cresol to a melt of 600 g of aluminum chloride and 120 g of sodium chloride at 120-130° yields a mixture of isomeric keto-acids. However, if the reaction mixture is heated at 165°, the product is a mixture of the corresponding anthraquinones.[81] Similarly, pyrocatechol and phthalic anhydride heated at 110° with a fused mass of $AlCl_3$-NaCl yields the keto-acid and not hystazarin, the corresponding anthraquinone [82]:



The condensation of phthalic anhydride with phenol in the presence of aluminum chloride and in the absence of solvent gives phenolphthalein if the phthalic anhydride and aluminum chloride are used in molecular proportions, and the phenol is in slight excess. The use of zinc chloride, a milder catalyst, gives better yields,[83] indicating that possibly phthalide formation is a function of reduced catalytic activity. Anhydrous ferric chloride, however, gives poorer yields than either the aluminum or zinc chloride, and results in a contaminated product. Using tetrachloroethane as a solvent, phenols yield hydroxybenzoylbenzoic acids.

As in other Friedel-Crafts reactions, cleavage of alkoxy- groups may occur during condensation of phenol ethers with phthalic anhydride. Scholl and Seer [84] observed that *p,p'*-dihydroxybiphenyl and *p,p'*-dimethoxybiphenyl both yield 4,4'-dihydroxy-3-(2''-carboxybenzoyl)-biphenyl when reacted with phthalic anhydride. On further heating of the reaction mixture to 130-135°C there is formed the dibasic acid, 4,4'-dihydroxy-3,3'-bis-(2''-carboxybenzoyl)biphenyl. The loss of a methyl group has also been noted with the naphthyl ethers. Whereas α-methoxynaphthalene gives a 91 per cent yield of 2-(4'-methoxynaphthoyl-1')-benzoic acid in tetrachloroethane as a solvent;[85] the use of carbon disulfide as solvent results also in formation of the corresponding demethylated product.[86]

[81] H. Waldmann and P. Sellner, *J. prakt. Chem.*, 150, 145-152 (1938); *C. A.*, 32, 4573.
[82] German P. 642,719 (1937) to H. Waldmann (to I. G.); *C. A.*, 31, 6261. Compare with work of F. Ullmann, P. 523.
[83] C. F. Ward, *J. Chem. Soc.*, 119, 830-832 (1921); *C. A.*, 15, 2862.
[84] R. Scholl and C. Seer, *Ber.*, 44, 1091-1103 (1911).
[85] L. F. Fieser and E. M. Dietz, *J. Am. Chem. Soc.*, 51, 3141-3148 (1929).
[86] R. Scholl, C. Seer, and A. Zinke, *Monatsh.*, 41, 583-602 (1921).

Table 25.

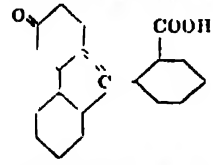
Phenol or Ether	Product	Ref
Phenol	2′ and 4′-hydroxy-2-benzoylbenzoic acids	1
p-Halogeno-phenol	5′-halogeno-2′-hydroxy-2-benzoylbenzoic acid	21
p-Chlorophenol	4-chloro-1-hydroxyanthraquinone	19
p-Cresol	1-hydroxy-4-methylanthraquinone	17
o-Cresol	2-hydroxy-3-methyl-, 1-methyl-2-hydroxy-, and 1-hydroxy-2-methyl anthraquinones	17
o-Cresol	4′-hydroxy-5′-methyl-2-benzoylbenzoic acid 2′-hydroxy-3′-methyl-2-benzoylbenzoic acid	1
m-Cresol	2′-hydroxy-4′-methyl-2-benzoylbenzoic acid 4′-hydroxy-6′-methyl-2-benzoylbenzoic acid	1
p-Cresol	2′-hydroxy-5′-methyl-2-benzoylbenzoic acid	1
p-Chloro-*o*-cresol	1-hydroxy-2-methyl-4-chloroanthraquinone	17
p-Chloro-*m*-cresol	2′-hydroxy-4′-methyl-5′-chloro-2-benzoyl-benzoic acid	1
Pyrocatechol	hystazarin	2
Pyrocatechol	3′,4′-dihydroxy-2-benzoylbenzoic acid	16
Hydroquinone	quinizarin	20
Pyrogallol	anthragallol	2
α-Naphthol	hydroxynaphthacenquinone	2
β-Naphthol	yellow compound, $C_{18}H_{10}O_3$	2, 4
4,4′-Dihydroxybiphenyl	4,4′-dihydroxy-3-(2″-carboxybenzoyl)biphenyl; 4,4′-dihydroxy-3,3′-bis(2″-carboxybenzoyl)-biphenyl; or 4,4′-dihydroxy-1,1′-bianthra-quinonyl at high temperatures	3
3,3′-Dihydroxybiphenyl		23
2,7-Dihydroxynaphthalene	a dihydroxybenzanthraquinone	2
1,4-Dihydroxynaphthalene	1,4-dihydroxy-2,3-benzanthraquinone	20
1,5-Dihydroxynaphthalene	7,15-dihydroxyhexacene-5,16,8,13-diquinone	24
Biresorcinol	2,4,2′,4′-tetrahydroxy-1,1′-bianthraquinonyl	3
1- or 2-Hydroxy-anthracenes	hydroxyquinones	2
Leucoquinizarin	1,4,5,8-tetrahydroxy-2,3,6,7-dibenzanthra-quinone (?)	2, 4
Anisole	4′-methoxy-2-benzoylbenzoic acid	8, 9
Chloroanisole	3′- or 5′-chloro-4′- or 2′-hydroxy-2-benzoyl-benzoic acid	18
Veratrole	3′,4′-dimethoxy-2-benzoylbenzoic acid	10
Pyrogallol trimethyl ether	2′,3′,4′ (or 3′,4′,5′)-trimethoxy-2-benzoyl-benzoic acid	11
2,6-Dimethoxytoluene	2′4′-dimethoxy-3′-methyl-2-benzoylbenzoic acid	12
p-Dimethoxybiphenyl	same products as for *p*-dihydroxybiphenyl	3
Diphenyl ether	4′-phenoxy-2-benzoylbenzoic acid	13, 14
Aryloxyalkyl halides, *e.g.*, phenoxyethoxyethyl chloride	4′-(β-chloroethoxyethoxy)-2-benzoylbenzoic acid	22
p-Tolyl ether	2-(2′-carboxybenzoyl)-4-methylphenyl 4-methylphenyl ether	15

Table 25—*Continued*

Phenol or Ether	Product	Ref.
β-Methoxynaphthalene	2-(2′-hydroxynaphthoyl-1′)-benzoic acid	4
α-Methoxynaphthalene	2-(4′-methoxynaphthoyl-1′)-benzoic acid 2-(4′-hydroxynaphthoyl-1′)-benzoic acid [note 6 gives both; note 5 only the methoxy- compound]	5, 6
2-Methoxy-1-methylnaphthalene	2-(2′-methoxy-1′-methylnaphthoyl-6′)-benzoic acid	7

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1 F. Ullmann and W. Schmidt, *Ber.*, 52, 2098-2113 (1919).
2 German P. 298,245 (1916) to Farbenfabriken vorm F. Bayer & Co.; *C. Z.*, 1917, II, 256
3 R. Scholl and C. Seer, *Ber.*, 44, 1091-1103 (1911).
4 L. F. Fieser, *J. Am. Chem. Soc.*, 53, 3546-3560 (1931).
5 L. F. Fieser and E. M. Dietz, *J. Am. Chem. Soc.*, 51, 3141-3148 (1929).
6 R. Scholl, C. Seer, and A. Zinke, *Monatsh.*, 41, 583-602 (1921).
7 R Scholl and W. Neuberger, *Monatsh.*, 33, 507-533 (1912).
8 C Nourrisson, *Bull. soc. chim.*, 46, (2), 203-208 (1886); *J. Chem. Soc. Abs.*, 50, 1029 (1886).
9 E. B. Barnett, N. F. Goodway, and L. H. W. Savage, *Ber.*, 64, 2185-2194 (1931).
10 K Lagodzinski, *Ann.*, 342, 90-111 (1905).
11 W H. Bentley and C. Weizmann *J. Chem Soc.*, 93, 435-438 (1908).
12 P. C. Mitter and H. Biswas, *J. Indian Chem. Soc.*, 7, 839-841 (1930); *Brit. Chem. Abs.*-A, 225 (1931).
13 E B. Barnett and N F. Goodway, *Ber.*, 63, 3048-3051 (1930).
14 H Kipper, *Brr.*, 38, 2490-2493 (1905).
15 J Reilly and P. J. Drumm. *J Chem. Soc*, 2814-2819 (1927).
16 German P. 642,719 (1937) to Hans Waldmann (to I. G.). *C. A.*, 31, 6261.
17 H. Waldmann and P. Bellner, *J. prakt chem.*, 150, 145-152 (1938); *C. A.*, 32, 4573.
18 M. Hayashi, *J. prakt. Chem. (2)*, 123, 289-312 (1929); *Brit. Chem. Abs.*-B, 89 (1930).
19 H Waldmann and W. Hartisch, *J prakt Chem. (2)*, 130, 93-102 (1931); *Brit. Chem. Abs.*-A, 846 (1931).
20 H. Raudnitz, *Ber.*, 62, 509-513 (1929)
21. British P. 14,954 (1914) to F. Ullmann; *J. Chem Abs.*, 108 (I), 1065 (1915).
22. U S P. 2,132,675 (1938) to H A. Bruson and J. W Eastes (to Röhm & Haas Co.); British P. 506, 301 (1939) to Röhm & Haas Co.
23 S Dutt, *J. Chem. Soc.*, 1171-84 (1926)
24. E. Clar, *Ber.*, 72, 1817-21 (1939); *C. A.*, 34, 753

β-Methoxynaphthalene with aluminum chloride yields 2-(2′-hydroxynaphthoyl-1′)-benzoic acid in tetrachloroethane solution.[87]

Condensations of phenols or phenol ethers with phthalic anhydride and aluminum chloride are listed in Table 25. Production of quinones indicates the use of high temperatures or fusion with an aluminum chloride-sodium chloride melt.

Aromatic Ketones and Carboxylic Acid Derivatives

Both the keto- and the carboxy- groups have an inhibiting effect on Friedel-Crafts condensations. However, this effect becomes less apparent with increasing aromaticity.

Two moles of phthalic anhydride seldom add to one mole of benzenoid hydrocarbon or its derivatives, whereas diacylation occurs often in condensations of acyl halides with polyalkylated or polyhydroxy- benzenes, or with polynuclear hydrocarbons.* In reactions with acyl halides, introduction of one acyl group prevents introduction of a second acyl group unless the aromaticity of the product is sufficient to activate further reaction. In phthalic anhydride reaction products, however, there is the combined inhibiting effect of a keto- group and a carboxylic acid group,

[87] L. F. Fieser, *J. Am. Chem. Soc.*, 53, 3546-3560 (1931).

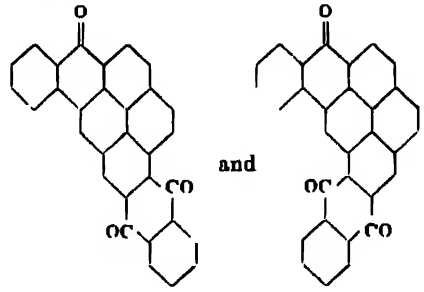
* See pages 222, 278 and 351.

so that the addition of two moles of the anhydride is not so common Disubstitution is also hindered by the fact that an excess of phthalic anhydride may lead to phthalides, and that the use of extreme conditions may result in ring closure of the primarily formed keto-acid.

Instances of reaction of phthalic anhydride with keto- or carboxy-compounds which have been reported deal with highly aromatic derivatives. Condensation of dihydroxy-1,4-dihydronaphthacenequinone with phthalic anhydride and aluminum chloride, followed by cyclization with $AlCl_3$-NaCl yields a hexacene derivative.[88] Leucoquinizarin in the presence of aluminum chloride at 250° yields what is probably 5,6,12,14-tetrahydroxypentacene-6,13-quinone.[89] Dibenzanthrones having positions 2:2′ free may be condensed in the presence of aluminum chloride or $AlCl_3+SbCl_3$ with phthalic anhydride to give vat dyes.[90]

A vat dye has been claimed as product of the reaction of (carboxybenzoyl)pyrene and phthalic anhydride in equimolecular proportions at a raised temperature in presence of aluminum chloride or an $AlCl_3$-NaCl melt.[91]

3-Benzoylpyrene with phthalic anhydride and $AlCl_3$-NaCl yields a mixture of the following ring ketones[92]:

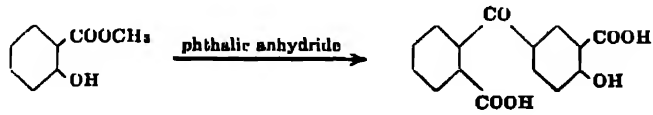


Condensation of phthalic anhydride may occur with a hydroxy- or methoxy- derivative of an anhydride of a highly aromatic acid. By heating a mixture of 3-hydroxynaphthalic anhydride and phthalic anhydride with aluminum chloride at 260°, reaction is effected to yield what is probably 4,5-bis(2′-carboxybenzoyl)-3-hydroxynaphthalic anhydride Reaction under milder conditions yields an intermediate product, probably 4-(2′-carboxybenzoyl)-3-hydroxynaphthalic anhydride.[93]

Esters of benzoic acid do not condense with phthalic anhydride; however, the presence of a hydroxy- group in the nucleus of the ester may enable reaction to occur. Heating for three to four hours at 125° a mixture of 10 g of phthalic anhydride, 10 g of methyl salicylate, and 25 g of

[88] C. Marschalk, *Bull. soc. chim. (5)* 5, 306-309 (1938); *C. A.*, 32, 4574.
[89] L. F. Fieser, *J. Am. Chem. Soc.*, 53, 3546-3560 (1931)
[90] U. S P. 2,058,477 (1936) to W. H Lycan (to du Pont); *Brit. Chem. Abs.*-B, 1153 (1937) cf U. S P. 2,058,606-7 (1936) to W. H. Lycan (to du Pont); *Brit. Chem. Abs.*-B, 1153 (1937).
[91] Brit P. 469,638 (1937) to Soc pour l'ind. chim. a Bale; *C A.*, 32, 797.
[92] R Scholl, K. Meyer, and J Donat, *Ber*, 70, 2150-2159 (1937); *Brit. Chem. Abs.*-A (II), 20 (1938)
[93] German P. 603,101 (1934) to A Riedel; *C. A.*, 29, 615.

aluminum chloride in 50 cc of tetrachloroethane yields 3'-carboxy-4'-hydroxy-2-benzoylbenzoic acid:



Ester hydrolysis also occurs in like reaction with the methyl ester of 2-hydroxy-3-methylbenzoic acid, the product in this case being 3'-carboxy-4'-hydroxy-5'-methyl-2-benzoylbenzoic acid.[94] As has been already noted, condensation of phthalic anhydride with phenols and phenol ethers occurs with introduction of the keto- group in the *ortho*-position to the hydroxy-; with esters of hydroxy- acids, however, addition takes place *para*- to the hydroxy-, and not *ortho*- to a hydroxy- or a carboxy- group.

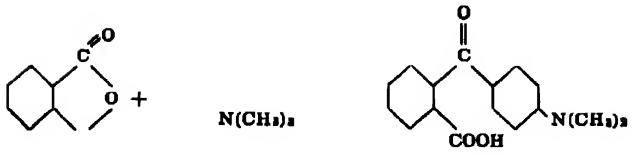
Nitrogenous Compounds

Nitro- compounds.—Although nitro- derivatives of hydrocarbons ordinarily undergo Friedel-Crafts reactions only when there is also present in the nucleus sufficiently activating groups to counteract the inhibiting effect of the nitro- group, or when the nitro- group is a substituent in a highly aromatic compound, nitrobenzene has been shown to react with tetrachlorophthalic anhydride. 2-(Nitrobenzoyl)tetrachlorobenzoic acid (m.p. 242-5°) is secured by adding aluminum chloride to a mixture consisting of 20 g of the anhydride and 300 cc of nitrobenzene and boiling for three hours.[95] A like reaction has not been reported with phthalic anhydride.

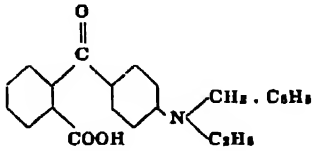
Another phthalic anhydride derivative which has been condensed with a nitro- derivative of benzene is 3,5-dimethoxyphthalic anhydride. Heating at 75° for twenty hours a mixture consisting of 10 g of 3,5-dimethoxyphthalic anhydride, 35 g of *o*-nitro-*m*-cresol, and 20 g of aluminum chloride results in a 62 per cent yield of 3,5-dimethoxy-2-(4-hydroxy-2-methyl-5-nitrobenzoyl)benzoic acid.[96]

Aryl amines.—In 1894, Haller and Guyot [97] reported that the reaction of dimethyl- or diethylaniline with phthalic anhydride and aluminum chloride in carbon disulfide leads to the formation of the corresponding dialkylamidobenzoic acid. Treatment of 45 g of the anhydride and 37 g of dimethylaniline in 200 g of carbon disulfide with 40 g of aluminum chloride and boiling until evolution of hydrogen chloride had ceased has been reported by Limpricht [98] to result in a 70 per cent yield of 4'-(dimethylamino)-2-benzoylbenzoic acid, according to the scheme:

[94] P. C. Mitter and H. C. Ray, *J. Ind. Chem. Soc.*, 9, 247-250 (1932); *C. Z.*, 1932, II, 3232.
[95] A. Hofmann, *Monatsh.*, 36, 805-824 (1915); *C. Z.*, 1916, 1, 105.
[96] G. D. Graves and R. Adams, *J. Am. Chem. Soc.*, 45, 2439-2455 (1923).
[97] A. Haller and A. Guyot, *Compt. rend.*, 119, 205-207 (1894); *J. Chem. Soc. Abs.*, 66 (I), 602 (1894); *Compt. rend.*, 126, 1248 (1898).
[98] H. Limpricht, *Ann.*, 300, 228-239 (1898).

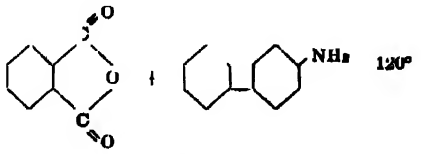


Condensation of benzylethylaniline under like conditions yields 4′-(ethylbenzylamino)-2-benzoylbenzoic acid [99]:

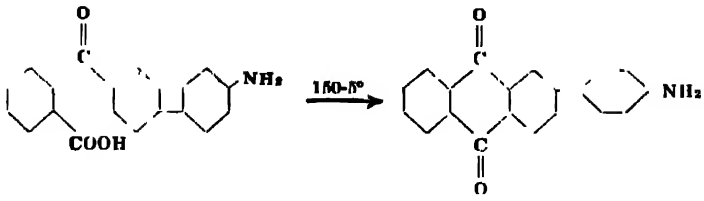


The reaction of polynuclear amines takes a similar course. β-Naphthylamine adds normally to phthalic anhydride in an $AlCl_3$-NaCl melt kept at 110-115° to yield an aminonaphthoylbenzoic acid.[100] Attempts to react 2-amino-1-methylnaphthalene, or its acetyl or phthaloyl derivatives, with phthalic anhydride and aluminum chloride in carbon disulfide have been reported to be unsuccessful.[101]

Kranzlein [102] has been successful, however, in preparing keto-acids from a number of polynuclear amines and phthalic anhydride reactants with an $AlCl_3$-NaCl melt at temperatures of 110-120°. Further heating at about 150° results in ring closure. Thus, 90 g of 4-aminobiphenyl were introduced with stirring into 1200 g of an $AlCl_3$-NaCl melt heated to 120°. Upon cooling to 110°, 80 g of phthalic anhydride was gradually added; during the addition, the temperature was not allowed to exceed 120°. The reaction mixture is then heated for fifteen minutes at 120° for the production of an almost quantitative yield of 4″-amino-4′-phenyl-2-benzoylbenzoic acid. If heating is continued for an hour and forty-five minutes longer at 150-155°, ring closure occurs, with formation of 2-(4-aminophenyl)anthraquinone. The yield of the crude quinone was 83 per cent, but only a 45 per cent yield of the pure compound could be secured. The reaction occurred according to the scheme:



[99] A. Haller and A. Guyot, *Bull. soc. chim. (3)*, 25, 165-174 (1901), *J. Chem. Soc. Abs.*, 80 (I), 276 (1901); German P. 114,197 to Soc. St. Denis, *C. Z.*, 1900, II, 883.
[100] German P. 680,230 to G. Kranzlein, A. Wolfram, L. Schornig, and W. Elbs (to I. G.), *C* 4, 32, 3257.
[101] R. Scholl, W. Neuberger, W. Tritsch, and J. Potschlwauschegg, *Monatsh.*, 33, 507-535 (1912), *J Chem. Soc. Abs.*, 102 (I), 562 (1912).
[102] P. Kranzlein, *Ber.*, 71, 2325-2333 (1938).

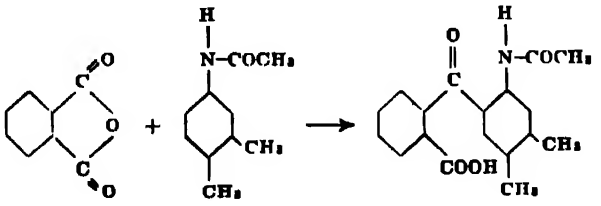


In this way the following compounds were prepared from the indicated aryl amines:

Aryl Amine	Product	% Yield of Pure Product
3-Methyl-4-aminobiphenyl	2-(3-methyl-4-aminophenyl)-anthraquinone	60
3-Aminophenanthrene	3-aminophthalylphenanthrene	..
2-Aminofluorene	2-aminophthalylfluorene	50–55
2-Aminochrysene	2-aminophthalylchrysene	
3-Aminopyrene	3-aminophthalylpyrene	

Like condensations could not be effected with either *m*-tolidine or benzidine, probably because the 4',4'-positions of these compounds are occupied.

Amides.—The preparation of amino-substituted keto-acids may also be readily effected by interaction of acetanilides with phthalic anhydride, and hydrolysis of the resulting acetamido- compound. When reaction is effected in solution, the use of a suitable solvent is of extreme importance. Carbon disulfide, ether, benzene, nitrobenzene, and *sym*-tetrachloroethane have all been investigated as solvents; the last gives the best results. 4-Acetamido-1,2-dimethylbenzene with phthalic anhydride in tetrachloroethane solution in the presence of aluminum chloride at 100° for one hour gives a 68 per cent yield of 2'-acetamido-4',5'-dimethyl-2-benzoylbenzoic acid [103]:



Analogously, acetamido- keto-acids were prepared from 2-acetamido-5,6,7,8-tetrahydronaphthalene, 5-acetamidohydrindene, and *m*-acetotoluidine in 46, 61, and 40 per cent yields, respectively. In every case the phthalic anhydride residue entered *ortho*- to the acetamido-group. Ring closure of the keto-acid from 4-acetamido-1,2-dimethylbenzene was easily effected by heating with sulfuric acid, but at the same time there was a 10 per cent conversion to lactam. Similar treatment of the other

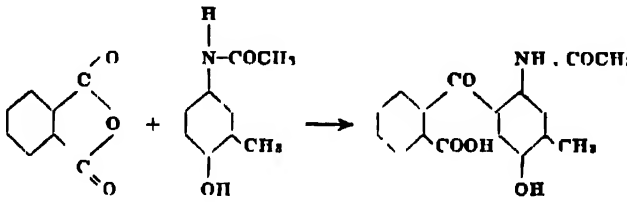
[103] P. Kranzlein, *Ber.*, **70**, 1963-1966 (1937).

keto-acids resulted in sulfonation, and heating with hydrochloric acid led to lactams.

The preparation of aminohydroxyanthraquinones has been claimed by heating phthalic anhydride with an amidophenol or its ether with an $AlCl_3$-NaCl melt at 100°, hydrolysis of the resulting amido keto-acid, and cyclization by treatment with sulfuric acid.[104] The following preparations are described:

Amidophenol or Ether	Product
2,2'-Dimethoxydiphenylurea	2-amino-3-hydroxyanthraquinone
1-Benzamido-4-phenol	1-amino-4-hydroxyanthraquinone
Phosgenated 1-amino-3-chloro-6-methoxybenzene	1-hydroxy-2-amino-4-chloro-anthraquinone
Phosgenated 1-amino-3-methyl-6-methoxybenzene	1-hydroxy-2-amino-4-methyl-anthraquinone

1-Acetamido-3-methyl-4-hydroxybenzene heated with phthalic anhydride for ten minutes at 110° in an $AlCl_3$-NaCl melt gives a 64 per cent yield of 2'-acetamido-4'-methyl-5'-hydroxy-2-benzoylbenzoic acid [105]:

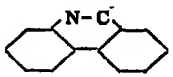


Similar treatment of 4-acetamidobiphenyl results in an 87 per cent yield of 4''-amino-4'-phenyl-2-benzoylbenzoic acid [105]

Nitrogen Ring Compounds.—Ring compounds of nitrogen are generally resistant to Friedel-Crafts reactions In the absence of a catalyst, in an inert diluent, phthalic anhydride reacts with picoline or quinaldine to yield phthalones, condensation probably taking place through the methyl group of the N-ring compound and the oxygen of the phthalic anhydride.[106]

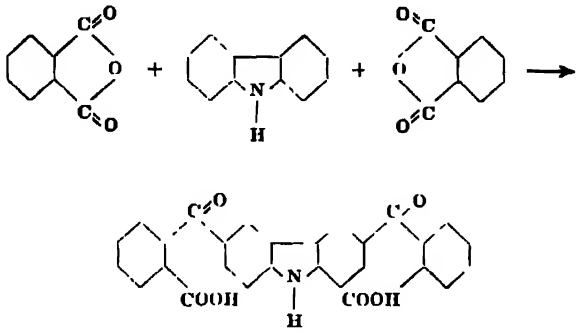
Jephcott [107] reports that phthalic anhydride with aluminum chloride and various addition compounds of pyridine and quinoline shows no reaction.

Condensation with production of keto-acids does occur with more highly aromatic ring compounds of nitrogen. Thus, phenanthridone



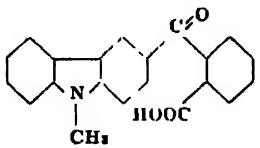
[104] British P. 337,047 (1930) to I. G. Farbenindustrie, *Brit. Chem. Abs.*-B, 195 (1931), *C. Z.*, 1932, I 131; German P. 538,467 (1931) to I. G., *C. Z.*, 1932, II, 1537.
[105] P. Kranslein, *Ber.*, 71, 2233-2235 (1938)
[106] U. S. P. 1,963,874 (1934) to National Aniline and Chemical Co.; R. Kon and F. Bär, *Ann.*, 516, 155-161 (1935).
[107] C. M. Jephcott, *J. Am. Chem. Soc.*, 50, 1189-1192 (1928); *C. A.*, 22, 1975.

condenses with phthalic anhydride in the presence of aluminum chloride at 180-230° to give two isomeric (carboxybenzoyl)phenanthridones,[108] and carbazole is so reactive that the condensation, with or without a diluent, leads to the introduction of two phthalic anhydride residues, with production of 3,6-bis(2-carboxybenzoyl)carbazole[109]:



Replacement of N-hydrogen also occurred, with formation of some 9-(2-carboxybenzoyl)-carbazole.

The condensation with N-methylcarbazole also yields mono- and di-substitution.[110] In benzene solution the main reaction product is the monobasic acid, together with the di-substituted derivative. Since no N-hydrogen is available, it was assumed that the product had the structure:



3,6-Bis(2-carboxybenzoyl)-9-methylcarbazole was the main reaction product when condensation was effected in carbon disulfide solution. The use of equimolecular quantities instead of two moles of phthalic anhydride tends to increase mono-substitution.[111]

Treatment of 9-ethylcarbazole with phthalic anhydride and aluminum chloride in nitrobenzene solution has been claimed to yield 3,6-bis(2-carboxybenzoyl)-9-ethylcarbazole.[112] It has been reported, however, that the use of nitrobenzene as a solvent gives only a 38 per cent yield of the dibasic acid, and that reaction is more readily effected by gradually add-

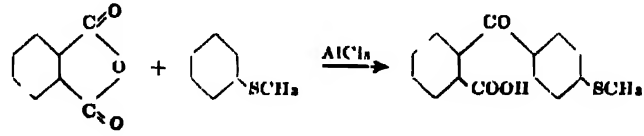
[108] British P. 306,488 (1929) to I. G. Farbenindustrie; *Brit. Chem. Abs.*-B, 755 (1930).
[109] R. Scholl and W. Neovius, *Ber.*, 44, 1249-1252 (1911); *J. Chem. Soc. Abs.*, 100 (I), 567 (1911); *cf.* R. Stilmmer, *Monatsh.*, 28, 411 (1907); *C. A.*, 1, 2373. D. R. Mitchell and S. G. P. Plant, *J. Chem. Soc.*, 1295-1298 (1936).
[110] F. Ehrenreich, *Monatsh.*, 32, 1103-1114 (1911); C. Z., 1912, I, 819.
[111] *cf.* M. Copisarow and C. Weizmann, *J. Chem. Soc.*, 107, 878-888 (1915).
[112] German P. 261,495 to L. Cassella & Co.; *J. Chem. Soc. Abs.*, 104 (I), 1098 (1913).

ing aluminum chloride to a mixture of 4 moles of phthalic anhydride and 1 mole of 9-ethylcarbazole in 20 moles of chlorobenzene.[113]

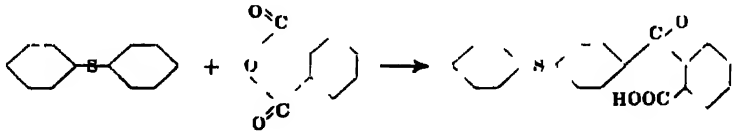
The condensation of phthalic anhydride with 2-aminocarbazole or with 3-amino-9-ethylcarbazole at 110° with an $AlCl_3$-NaCl catalyst gives 2-amino- and 3-amino-9-ethylphthalylcarbazole in 65-70 per cent and 52 per cent yields, respectively.[114]

Sulfur Compounds

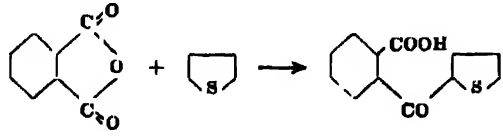
Thioethers.—Methyl phenyl sulfide has been shown to undergo addition to phthalic anhydride. Treatment of a mixture consisting of 25 g of the sulfide and 15 g of the anhydride with 30 g of aluminum chloride, with subsequent heating for four hours at 80° gives 22 g of the methyl ether of 4'-mercapto-2-benzoylbenzoic acid.[115]



Upon boiling for four hours a carbon disulfide solution of 22.3 g of diphenyl sulfide, 45 g of phthalic anhydride, and 48 g of aluminum chloride, a 25 g yield of 4-(2-carboxybenzoyl)phenyl phenyl sulfide is secured.[116]



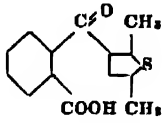
Ring Compounds of Sulfur.—In carbon disulfide solution, 18 g of phthalic anhydride condenses with 10 g of thiophene upon heating with 27 g of aluminum chloride to give 5-7 g of 2-(2-thenoyl)benzoic acid [117].



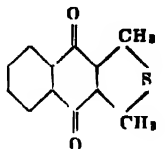
Upon heating with sulfuric acid or with phosphorus pentoxide, the acid is converted in small yield into thiophanthrenequinone.

[113] V. A. Ignatyuk-Malstrenko and N. S. Tikhonov, *Anilinokrasochnaya Prom.*, 4, 473-475 (1934); *C. A.*, 29, 1069; Russian P. 35,189 (1934) to N. S. Tikhonov and V. A. Ignatyuk-Malstrenko; *C. A.*, 30, 3448.
[114] P. Kranzlein, *Ber.*, 71, 2228-2235 (1938).
[115] F. C. Halin and E. E. Reid, *J. Am. Chem. Soc.*, 46, 1645-1653 (1924).
[116] R. Scholl and C. Seer, *Ber.*, 44, 1233-1249 (1911).
[117] W. Steinkopf, *Ann.*, 407, 94-108 (1914); *J. Chem. Soc. Abs.*, 106 (I), 153 (1914); *cf.* F. Ernst, *Ber.*, 19, 2378-2382 (1886).

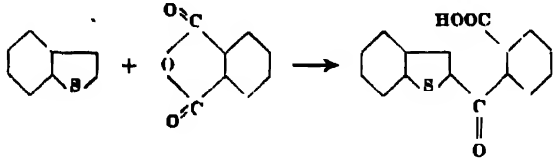
The condensation of 2,5-thioxene with phthalic anhydride in nitrobenzene solution upon treatment with aluminum chloride at 0-5° gives a 62 per cent yield of 2-(2,5-dimethyl-3-thenoyl)benzoic acid [118]:



Upon heating with sodium chloride and aluminum chloride, conversion to 2,7-dimethyl-β-thiophanthrenequinone occurs.



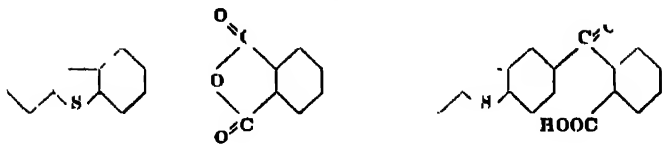
2,3-Phthalylthianaphthenes are obtained by condensation of thianaphthenes with phthalic anhydride or its derivatives in the presence of aluminum chloride, and subsequent cyclization by treatment with thionyl chloride and aluminum chloride.[119] Thianaphthene is not completely stable against aluminum chloride, so that yields are low. Thus, upon gradual addition of thianaphthene in nitrobenzene solution to a cold mixture of phthalic anhydride and aluminum chloride in nitrobenzene, and subsequent stirring for three days, only a 35 per cent yield of 2-(2-thianaphthenoyl)benzoic acid is secured [120]:



Better results are secured with substituted thianaphthenes. Like treatment of 4-methyl-6-chlorothianaphthene gives a 62 per cent yield of 2-(4-methyl-6-chloro-2-thianaphthenoyl)benzoic acid.

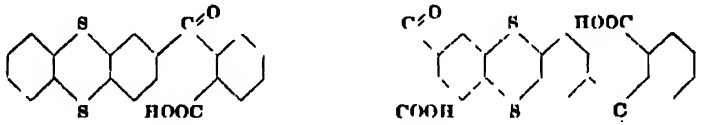
Dibenzothiophene has been converted with good yields into the corresponding keto-acid. Treatment of a suspension of 92 g of dibenzothiophene and 82 g of phthalic anhydride with 150 g of aluminum chloride at 0-5° results in the production of 135 g of crude 2-(2-dibenzothenoyl)benzoic acid [121]:

[118] W. Steinkopf, T. Bariag, and H. J. v. Petersdorff, *Ann.*, 540, 7-14 (1939).
[119] British P. 266,189 (1927) to I. G. Farbenindustrie; *Brit. Chem. Abs.*-B, 635 (1928); *cf.* Brit. P. 261,383; German P. 499,745 to I. G.
[120] F. Mayer, *Ann.*, 426, 276 (1921); *Brit. Chem. Abs.*-A, 1163 (1921).
[121] H. Gilman and A. L. Jacoby, *J. Org. Chem.*, 3, 108-119 (1938); *C. A.*, 33, 579.



The behavior of dibenzothiophene thus differs from that of carbazole, its nitrogen analog, in that carbazole adds to two moles of phthalic anhydride, giving the dicarboxylic acid.[122]

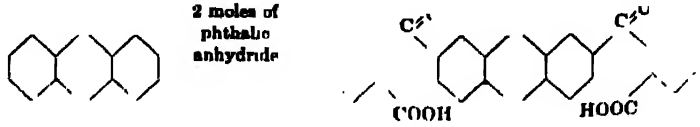
Thianthrene gives a mixture of mono- and di-substitution products.[123] When a carbon disulfide solution of 4 g of thianthrene, 6 g of phthalic anhydride, and 10 g of aluminum chloride is heated for eight hours there is obtained a mixture consisting of 3.4 g of 2-(2-thianthrenoyl)benzoic acid (I) and about one-fourth that amount of 3,8-bis(2-carboxybenzoyl)-thianthrene (II).



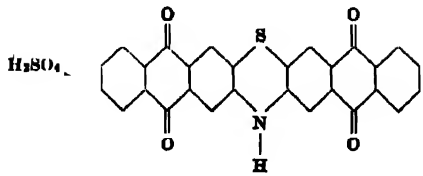
(I) (II)

The yield of the dicarboxylic acid is increased to 4.5 g when thianthrene is treated with about 3 parts of phthalic anhydride, and the boiling continued for 24 hours. 3,8-Dimethylthianthrene and 5 parts of phthalic anhydride treated for about two hours at 60-100° with 10 parts of aluminum chloride and then heated for seven hours at 100-104° gives a 73 per cent yield of 2,7-bis(2-carboxybenzoyl)-3,8-dimethylthianthrene.

Phenothiazine gives a dibasic acid, the two entering groups being introduced in the *p*-positions with respect to the imino- group, and a small amount of a tribasic acid in which the carboxybenzoyl residue is also attached at the nitrogen. Reaction was effected by boiling under reflux for six hours a solution of 2 g of phenothiazine, 4 g of phthalic anhydride, and 5.5 g of aluminum chloride. There was secured an 0.8 g yield of 3,7-bis(2-carboxybenzoyl)phenothiazine which, upon ring closure with sulfuric acid, yields 3,2:8,7-diphthalylphenothiazine[123]:



[122] R. Scholl and W. Neovius, *Ber.*, 44, 1249-1252 (1911).
[123] R. Scholl and C. Seer, *Ber.*, 44, 1253-1269 (1911); *C. A.*, 5, 2054.

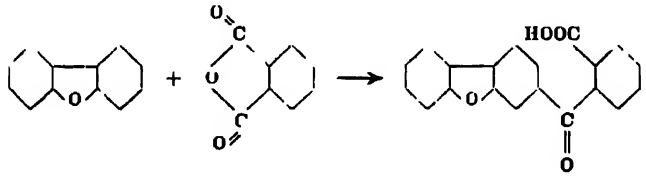


The poor yield of the keto-acid was ascribed to the fact that the aluminum chloride became embedded in the viscous reaction mixture. When the condensation is effected without a solvent at 105°, the closed ring compound is obtained directly.

N-methylphenothiazine under similar treatment gave only disubstitution.

Oxygen Ring Compounds

Condensation of dibenzofuran with phthalic anhydride and aluminum chloride has been reported to result in the formation of a keto-acid, probably 3-(2-carboxybenzoyl)dibenzofuran [124]:



Fusion of 3-aminodibenzofuran and phthalic anhydride with an $AlCl_3$-NaCl melt for thirty minutes at 115° and then for 1½ hours at 150° leads to the production of the closed ring compound, 3-aminophthalyldibenzofuran in 40 per cent yield.[125]

Dibenzodioxane or its mono-chloro- derivative has been claimed to condense with phthalic anhydride to give the corresponding keto-acids. Addition of aluminum chloride to a solution of dibenzodioxane in chlorobenzene at 10-15° gives a 98 per cent yield of 2-dibenzodioxanoylbenzoic acid.[126]

Substituted Phthalic Anhydrides

Halogenated Phthalic Anhydrides.—These derivatives of phthalic anhydride have been employed frequently for the preparation of halogenated keto-acids. In 1879 von Pechmann [127] reacted bromophthalic anhydride and benzene with aluminum chloride to obtain what he called o-bromobenzoylbenzoic acid. Stephens [128] has pointed out that von Pechmann used a mixture of anhydrides and should have obtained four acid products. He considered the product obtained to be 2-bromo-6-benzoyl-

[124] R. Stümmer, *Monatsh.*, 28, 411-422 (1907); *C. A.*, 1, 2373
[125] P. Kranzlein, *Ber.*, 71, 2328-2335 (1938).
[126] German P. 668,575 (1938) to H. Wechse and W. Eckardt, *C. A.*, 33, 5006.
[127] H. von Pechmann, *Ber.*, 12, 2124-2129 (1879).
[128] H. N. Stephens, *J. Am. Chem. Soc.*, 43, 1950-1956 (1921).

benzoic acid. Using pure reactants, Stephens observed that 3-bromophthalic anhydride with benzene and aluminum chloride gave only 2-bromo-6-benzoylbenzoic acid, whereas the 4-bromo- derivative gave about equal amounts of 3-bromo-6-benzoylbenzoic acid and 4-bromo-2-benzoylbenzoic acid in a total yield of 97 per cent. In the presence of acetic anhydride, a condition which is favorable to diphenylphthalide formation,[129] it was noted that the 3-bromo- anhydride did not form a diphenylbromophthalide, whereas the 4-bromo- anhydride gave two such derivatives.

Waldmann and co-workers[130] extended the reaction with 4-bromophthalic anhydride to prepare derivatives of bromobenzene, chlorobenzene, naphthalene, and chloronaphthalene, and they secured 4,4'-dibromo-2-benzoyl-, 4'-chloro-4-bromo-2-benzoyl-, 4-(or 5)-bromo-2-naphthoyl-, and 4'-chloro-4-(or 5)-bromo-2-naphthoylbenzoic acids, respectively. In an analogous manner derivatives were prepared by reacting 4-chlorophthalic anhydride with bromobenzene and chloronaphthalene. Products of the reaction between chlorinated phthalic anhydride and chlorobenzene may be further treated to produce chloroaminoanthraquinones and indanthrones.[131]

Treatment of 3-hydroxynaphthalic anhydride with 4-chlorophthalic anhydride is claimed to give a chloro-4,5-phthalyl-3-hydroxynaphthalic anhydride, useful as a dye intermediate.[132]

Upon addition, in one portion, of 85 g of aluminum chloride to a mixture of 60 g of finely powdered 3,6-dichlorophthalic anhydride and 250 g of benzene, allowing the reaction mixture to stand for two hours, heating on an oil-bath for four hours while the temperature increases to 90°, and then holding it at that temperature for two to three hours, a 97.3 per cent of theoretical yield of crude 3,6-dichloro-2-benzoylbenzoic acid (m.p. 165-166°) is obtained.[133] Like reaction with 3,4-dichlorophthalic anhydride gives a 96 per cent of theoretical yield of 3,4- (or 5,6-)dichloro-2-benzoylbenzoic acid; with 4,5-dichlorophthalic anhydride, a 98 per cent yield of 4,5-dichloro-2-benzoylbenzoic acid is similarly secured.[133]

3,6-Dichlorophthalic anhydride with toluene and aluminum chloride in carbon disulfide yields 4'-methyl-3,6-dichloro-2-benzoylbenzoic acid, m.p. 156°.[134]

Diiodophthalic anhydrides condense readily with benzene to give the correspondingly iodinated benzoylbenzoic acids.[135] Reaction is effected by refluxing for 24 hours a mixture consisting of 5 g of the diiodophthalic anhydride, 3.65 g of aluminum chloride, and 40 ml of benzene. The indicated anhydrides thus give the following keto-acids:

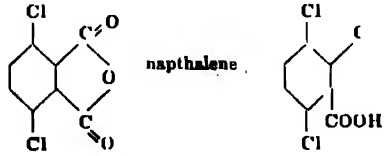
[129] H. von Pechmann, *Ber.*, 14, 1865-1867 (1881).
[130] H. Waldmann, *J. prakt. Chem.*, 126, 65-68 (1930). H. Waldmann and H. Mathiowetz, *J. prakt. Chem.*, 126, 69-75 (1930). H. Waldmann and G. Stenkal, *J. prakt. Chem.*, 127, 201-209 (1930).
[131] British P. 358,078 (1930) to J. Thomas, R. F. Thomson, W. Smith, and Imperial Chem. Ind., *C. A.*, 26, 5969.
[132] German P. 503,101 (1934) to A. Riechs; *C. A.*, 29, 615.
[133] F. Ullmann and C. Billig, *Ann.*, 381, 11-28 (1911); *cf.* A. Le Royer, *Ann.*, 238, 350-361 (1887). V. Villiger, *Ber.*, 42, 3529-3549 (1909).
[134] A. Le Royer, *loc. cit.*; V. Villiger, *loc. cit.*
[135] R. W. Higgins and C. M. Suter *J. Am. Chem. Soc.* 51, 2662-2664 (1929).

Diiodophthalic anhydride	-diiodobenzoic acid secured	m.p. (°C)	% Yield
4,5-	2-benzoyl-4,5-	244–5	80
3,4-	2-benzoyl-3,4-(?)	223–4	65
3,6-	2-benzoyl-3,6-	218–220	60

Anisole and the methyl ethers of *o*- and *m*-cresol were found to react readily with 4,5-diiodophthalic anhydride, but it was found impossible to bring about reaction between the anhydride and veratrole or chloroveratrole.[135]

3,6-Dichlorophthalic anhydride and *o*-xylene in the presence of aluminum chloride yields 3,6-dichloro-2-(2,3-dimethylbenzoyl)benzoic acid, m.p. 181°. *m*-Xylene gives 3,6-dichloro-2-(2,3-dimethylbenzoyl)benzoic acid (m.p. 164°) and *p*-xylene gives 3,6-dichloro-2-(2,5-dimethylbenzoyl)benzoic acid, m.p. 152°.[136] Good yields of the dichlorodimethylbenzoylbenzoic acids were obtained.

According to Graebe and Peter,[137] the condensation of 18 g of 3,6-dichlorophthalic anhydride with 25 g of naphthalene and aluminum chloride yields 8 g of 3,6-dichloro-2-α-naphthoylbenzoic acid, m.p. 207.5°:



More recently, Waldmann,[138] reacted 4,5-dichlorophthalic anhydride under like conditions and reported the ready production of 4′,5′-dichlorophenyl naphthyl ketone-2′-carboxylic acid, also melting at 207.5°. If the identical melting point is not a coincidence, either a migration of halogen during the reaction or a misnomer of the halogenated anhydrides used must be assumed.

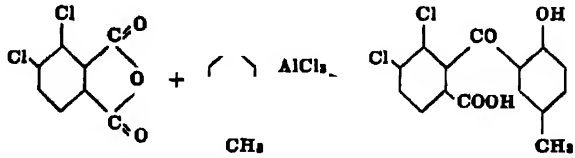
3,6-Dichlorophthalic anhydride with chlorobenzene and aluminum chloride yields 3,6-dichloro-2-(4-chlorobenzoyl)benzoic acid.[139]

Although *p*-dichlorobenzene reacts with difficulty in Friedel-Crafts reactions, it has been condensed with 3,6-dichlorophthalic anhydride. Upon heating 3.6 g of the anhydride with 250 g of dichlorobenzene at 180° until solution occurs, subsequent addition of 50 g of aluminum chloride, and heating at 200° for two hours, 3,6-dichloro-2(2,5-dichlorobenzoyl)-benzoic acid is obtained. It is converted upon heating with concentrated sulfuric acid into 1,4,5,8-tetrachloroanthraquinone.[140]

In the condensation of *p*-cresol with 3,6-dichloro- or 3,4-dichlorophthalic anhydride, the anhydride residue is attached to the carbon in *ortho*- position to the hydroxy. Reaction of 3,6-dichlorophthalic anhydride with *p*-cresol and aluminum chloride in *sym*-tetrachloroethane gives

[135] D. Harrop, R. V. Norris, and C. Weizmann, *J. Chem. Soc.*, **95**, 1312-1319 (1909).
[136] C. Graebe and W. Peter, *Ann.*, **340**, 259-266 (1905); *J. Chem. Soc. Abs.*, **88** (1), 704 (1905).
[137] H. Waldmann, *J. prakt. Chem.*, 131, 71-81 (1931); *C. A.*, **25**, 4878.
[138] S. Jaroschy, *Monatsh.*, **34**, 1-6 (1913); *C. A.*, **7**, 990.
[139] A. Hofmann, *Monatsh.*, **36**, 805-824 (1915); *C. Z.*, 1916, I, 104.

an 82.8 per cent yield of 2'-hydroxy-5'-methyl-3,6-dichloro-2-benzoylbenzoic acid. With 3,4-dichlorophthalic anhydride, analogous condensation gives 2'-hydroxy-5'-methyl-3,4-dichloro-2-benzoylbenzoic acid [141]:



Upon heating 4-chloro-*m*-cresol with 4,5-dichlorophthalic anhydride and aluminum chloride, 4,5-dichloro-2-(5-chloro-2-hydroxy-4-methylbenzoyl)benzoic acid is obtained.[142]

Hydroquinone reacts with 3,6-dichlorophthalic anhydride at 200° with a melt of $AlCl_3$-NaCl to give an 84 per cent yield of 5,8-dichloroquinizarin; the 4,5-dichloro- acid anhydride similarly gives an 80 per cent yield of 6,7-dichloroquinizarin.[143]

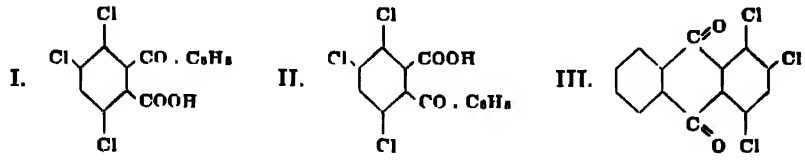
In the condensation of tolyl methyl ethers with 3,6-dichlorophthalic anhydride, hydrolysis of alkoxy- occurs with *p*- and *m*-tolyl methyl ethers. Upon gradual addition of 300 g of aluminum chloride to a mixture of 180 g of 3,6-dichlorophthalic anhydride and 100 g of *p*-tolyl methyl ether, and subsequent heating on a water-bath for eight hours, 3,6-dichloro-2-[5(or 6)-hydroxy-2(or 3)-methylbenzoyl]benzoic acid was secured. During the reaction, partial conversion to the corresponding quinone occurred. *o*-Tolyl methyl ether under like treatment yields 3,6-dichloro-2-[3(or 2)-hydroxy-2(or 3)-methylbenzoyl]benzoic acid. Similar reaction with *m*-tolyl methyl ether yields the unhydrolyzed product, 3,6-dichloro-2-[4(or 2)-methoxy-2(or 4)-methylbenzoyl]benzoic acid. A small amount of a substance, apparently formed by the condensation of 2 moles of the ether with 1 mole of the anhydride, was also isolated.[144]

Dialkylanilines react with dihalogenated phthalic anhydrides to give the corresponding keto-acids. Addition of 3,6-dibromophthalic anhydride to dimethylaniline in carbon disulfide solution in the presence of aluminum chloride occurs with the production of 3,6-dibromo-2-(4-dimethylaminobenzoyl)benzoic acid in 70 per cent yield.[145]. Like reaction with diethylaniline gives the analogous keto-acid. 3,6-Dichlorophthalic anhydride with dimethyl- or diethylaniline under the same conditions gives the corresponding chloro derivatives.[146]

3,4,6-Trichlorophthalic anhydride heated with 6 to 8 parts of benzene and 1½ parts of aluminum chloride yields 3,4,6- (or 3,5,6-) trichloro-2-

[141] A. M. v. dem. Kneesbeck and F. Ullmann, *Ber.*, 55, 306-316 (1923).
[142] German P. 283,493 (1915) to F. Ullmann; *C. Z.*, 1915, I, 643.
[143] H. Waldmann and H. Mathiowetz, *J. prakt. Chem.*, 126, 250-256 (1930).
[144] G. M. Walsh and C. Weizmann, *J. Chem. Soc.*, 97, 685-692 (1910).
[145] E. C. Severin, *Ann. Scient. Univ. Jassy*, 4, 141-150; *C. Z.*, 1907, I, 1121; *Compt. rend.*, 142, 1274-1276 (1906).
[146] E. C. Severin, *Compt. rend.*, 130, 723 (1900); *Bull. soc. chim. (3)*, 23, 876, 887 (1900); *ibid. (3)*, 25, 499 (1901).

benzoylbenzoic acid.[147] Since both the 3,4,6- or 3,5,6-trichloro- keto acids would give 1,2,4-trichloroanthraquinone (III) upon cyclization with sulfuric acid, the structure of the keto-acid was not established, but was assumed to be either I or II:



Triiodophthalic anhydrides have likewise been condensed with benzene.[148] From 3,4,6-triiodophthalic anhydride (0.061 mole), 18.1 g (0.136 mole) of aluminum chloride, and 200 ml of benzene after 21 hours of refluxing was obtained 37 g of a crude mixture of isomeric keto-acids in practically equal amounts. The acids were assumed to be 2-benzoyl-3,4,6- and 3,5,6-triiodobenzoic acids, both having the empirical formula $C_{14}H_7O_3I_3$.

Condensations of tetrahalogenated phthalic anhydrides with aromatic compounds are summarized in Table 26.

The presence of four negative substituents in tetrahalogenated phthalic anhydrides has a highly activating effect on their reactivity in Friedel-Crafts condensations. Good yields of the *o*-aroyl-tetrahalogeno-benzoic acids are obtained, and reaction proceeds with the formation of one acid product. Accordingly, it has been suggested that the condensation affords a means of identifying aromatic hydrocarbons.[149] Further differentiation in melting points may be secured by conversion of the keto-acids into quinones.

That tetrachlorophthalic anhydride is unusually active is evident from the fact that it has been condensed not only with *p*-dichlorobenzene, which is ordinarily inactive in Friedel-Crafts reactions, but also with trichlorobenzene and with nitrobenzene, two compounds which are even more resistant to condensations of this type. The reaction with 1,2,4-trichlorobenzene is effected by heating 30 g of the halogenated benzene with 15 g of the anhydride and 15 g of aluminum chloride for five hours at 150°. Condensation of tetrachlorophthalic anhydride with nitrobenzene is secured by addition of aluminum chloride to a solution of 20 g of the anhydride in 300 cc of nitrobenzene and subsequent boiling for three hours.

Condensation of tetrahalogenated phthalic anhydrides with aromatic hydrocarbons and aluminum chloride and subsequent treatment with acetic anhydride yields phthalides.[150] Tetrabromophthalic anhydride heated for nine hours at 80° with aluminum chloride in benzene and then

[147] C. Graebe and S. Rostowsew, *Ber.*, **34**, 2107-2113 (1901).
[148] R. W. Higgins and C. M. Suter, *J. Am. Chem. Soc.*, **61**, 2062-2064 (1939).
[149] H. W. Underwood and W. L. Walsh, *J. Am. Chem. Soc.*, **57**, 940-942 (1935).
[150] W. A. Lawrance and H. G. Oddy, *J. Am. Chem. Soc.*, **44**, 329-330 (1922); *C. A.*, **16**, 1379; *cf.* section on mechanism of Friedel-Crafts reactions with phthalic anhydrides, p. 513.

Table 26

Tetrahalogenated phthalic anhydride	Other reactant	-benzoic acid secured	m.p. (°C)	Ref
Chloro	benzene	3,4,5,6-tetrachloro-2-benzoyl- (98% yield)	200	1, 2
Bromo	benzene	3,4,5,6-tetrabromo-2-benzoyl-	230–2	6
Iodo	benzene	3,4,5,6-tetraiodo-2-benzoyl-	230–1	6, 12
Chloro	toluene	3,4,5,6-tetrachloro-2-(4-methylbenzoyl)- (94% yield)	174.5	3
Bromo	toluene	3,4,5,6-tetrabromo-2-(4-methylbenzoyl)- (89% yield)	212	3
Iodo	toluene	3,4,5,6-tetraiodo-2-(4-methylbenzoyl)- (91% yield)	266	3
Chloro	*o*-xylene	3,4,5,6-tetrachloro-2-(2,3-dimethylbenzoyl)-	177.5–8.5	4
Chloro	*m*-xylene	3,4,5,6-tetrachloro-2-(2,4-dimethylbenzoyl)-	222–4	4
Chloro	*p*-xylene	3,4,5,6-tetrachloro-2-(2,3-dimethylbenzoyl)-	244–6	4
Chloro	ethylbenzene	2-(4-ethylbenzoyl)tetrachloro-	172–3	4
Chloro	naphthalene	3,4,5,6-tetrachloro-2-α-naphthoyl- (78% yield)	229	5
Chloro	chlorobenzene	3,4,5,6-tetrachloro-2-(4-chlorobenzoyl)-	162–5	6
Bromo	bromobenzene	3,4,5,6-tetrabromo-2-[4(?)-bromobenzoyl]-	228–30	6
Chloro	*p*-dichlorobenzene	3,4,5,6-tetrachloro-2-(2,5-dichlorobenzoyl)-	238–9	6
Bromo	*p*-dichlorobenzene	3,4,5,6-tetrabromo-2-(2,5-dichlorobenzoyl)-	240–5	6
Bromo	*p*-dibromobenzene	3,4,5,6-tetrabromo-2-(2,5-dibromobenzoyl)-	218–9	6
Chloro	1,2,4,trichlorobenzene	3,4,5,6-tetrachloro-2-[2,3,5(or 2,4,5)-trichlorobenzoyl]-	226–230	7
Chloro	phenol	3,4,5,6-tetrachloro-2-(2-hydroxybenzoyl)- (78.9% yield)	216–218	8
Chloro	*m*-cresol	3,4,5,6-tetrachloro-2-(2-hydroxy-4-methylbenzoyl)- (76.6% yield)	226–8	8
Chloro	*p*-cresol	3,4,5,6-tetrachloro-2-(6-hydroxy-3-methylbenzoyl)- (84.8% yield)	232–5	8, 9
Chloro	*o*-cresol	3,4,5,6-tetrachloro-2-(2-hydroxy-3-methylbenzoyl)- (76.6% yield)	219–222	8
Chloro	β-naphthol	2′-hydroxy-3,4,5,6-tetrachloro-2-α-naphthoyl- (95.7% yield)	214–7	8 13
Chloro	anisole	3,4,5,6-tetrachloro-2-(4-methoxybenzoyl)-	182	10
Chloro	β-naphthyl methyl ether	tetrachloro(methoxynaphthoyl)	204	13
Chloro	dimethylaniline	(dimethylaminobenzoyl)tetrachloro-	211	11

Table 26—*(Continued)*

Tetra-halogenated phthalic anhydride	Other reactant	-benzoic acid secured	m.p. (°C.)	Ref.
Chloro	diethylaniline	(diethylaminobenzoyl)tetra-chloro-	222	11
Chloro	nitrobenzene	(nitrobenzoyl)tetrachloro-	242–5	6
Chloro	nitro-2,4-dichloro-benzene	an alkali-insoluble resin		6
Chloro	o-chloronitro-benzene	no reaction		

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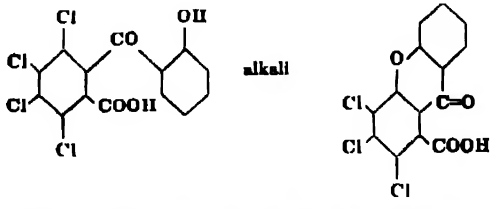
1. G. Kircher, *Ann.*, **238**, 338–349 (1887).
2. H. Meyer, *Monatsh.*, **25**, 1139 (1904).
3. W. A. Lawrance, *J. Am. Chem. Soc*, **43**, 2577–2581 (1921).
4. H. W. Underwood and W. L. Walsh, *J. Am. Chem. Soc*, **57**, 940–942 (1935).
5. C. Graebe and W. Peter, *Ann.*, **340**, 259–266 (1905); *J. Chem. Soc Abs.*, **88** (I), 704 (1905).
6. A. Hofmann, *Monatsh*, **36**, 805–825 (1915); *C. Z.*, **1916** I, 104.
7. A. Eckert and K. Steiner, *Monatsh.*, **36**, 269–280 (1915); *C. A.*, **9**, 1761.
8. F. Ullmann and W. Schmidt, *Ber.*, **52**, 2098–2118 (1919).
9. German P. 292,066 (1916) to F. Ullmann; *C. Z.*, **1916** I, 1211.
10. W. R. Orndorff and R. R. Murray, *J. Am. Chem. Soc.*, **39**, 879–897 (1917).
11. A. Haller and H. Umbgrove, *Compt. rend.*, **129**, 90–92 (1899); *J. Chem. Soc. Abs.*, **76** (I), 814 (1899).
12. A. Eckert and M. Klinger, *J. prakt Chem. (2)*, **121**, 281–288; *C. Z.*, **1929** II, 41.
13. A. Rieche and K. Jungholt, *Ber.*, **64**, 578–589 (1931).

three hours longer with acetic anhydride gives 94 per cent of diphenyltetrabromophthalide. Like reaction with toluene, instead of benzene, gives 93 per cent of the ditolyl homolog. Tetraiodophthalic anhydride gives poorer results in analogous condensations; diphenyltetraiodophthalide is secured in 61 per cent yield, and the corresponding ditolyl compound in 42 per cent yield.

As can be seen in Table 26, condensations with tetraiodophthalic anhydride and aromatic hydrocarbons occur normally with production of tetraiodo keto-acids. However, difficulty has been experienced in attempted ring closure to quinones because of liberation of iodine upon treatments of the keto-acids with either sulfuric acid or aluminum chloride.[151]

Upon heating with alkali, ring closure of tetrahalogenated hydroxy keto-acids may occur through replacement of the halogen *ortho-* to the carbonyl group. 3,4,5,6-Tetrachloro-2-(2-hydroxybenzoyl)benzoic acid thus yields trichloroxanthone-carboxylic acid [152]:



[151] A. Eckert and M. Klinger, *J. prakt. Chem. (2)*, **121**, 281–288; *C. Z.*, **1929**, II, 41.
[152] F. Ullmann and W. Schmidt, *Ber.*, **52**, 2098–2118 (1919).

The keto-acid obtained from tetrachlorophthalic anhydride and β-naphthol undergoes like ring closure.[152,153]

Nitrophthalic Anhydrides.—Friedel-Crafts condensations with nitrophthalic anhydrides are often complicated by the formation of isomeric keto-acids. Although yields are not good, the reaction has been studied as a means of preparing amino- and (through the amino-) the hydroxy-keto acids.

According to Lawrance,[154] reaction of 6.5 g of 3-nitrophthalic anhydride with 100 cc of benzene and 9 g of aluminum chloride, effected by heating the reactants for from four to five hours on a water-bath, results in the production of 1.7 g of a black resinous mass, 0.7 g of 6-nitro-2-benzoylbenzoic acid, and 0.6 g of 3-nitro-2-benzoylbenzoic acid. Like reaction with 6.5 g of 4-nitrophthalic anhydride was reported to give 0.8 g of 5-nitro-2-benzoylbenzoic acid and 0.5 g of the 2,4-isomer. Half of the anhydride used was recovered unchanged.

The condensation of 3-nitrophthalic anhydride with toluene was similarly shown to proceed with formation of two isomeric acids, 6-nitro-2-(4-methylbenzoyl)benzoic acid and the 2,3-isomer being secured. 4-Nitrophthalic anhydride, however, yielded only 4-nitro-2-(4-methylbenzoyl)-benzoic acid.[154]

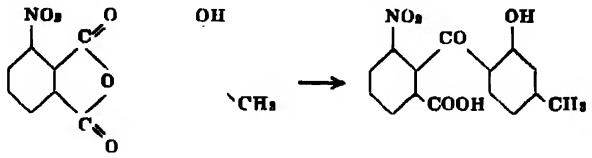
However, when Mitter and Sarkar[155] gradually added 15 g of aluminum chloride to a suspension of 3-nitrophthalic anhydride in toluene, and then heated the reaction mixture for five hours at 40-50° they secured only one product, 3-nitro-2-(4-methylbenzoyl)benzoic acid in 33 per cent yield. With 4-nitrophthalic anhydride and toluene the keto-acid previously secured by Lawrance was obtained. According to Mitter and Sarkar, the use of anhydrous aluminum chloride is conducive to resinification; better results are obtained when a slightly hydrated catalyst is used, or when a drop of water is added to the reaction mixture. The products secured by Lawrance were probably impure; their melting points did not agree with those reported by Mitter and Sarkar.

Only one acid, 3,5-dinitro-2-(4-methylbenzoyl)benzoic acid, is obtained in analogous condensation of 3,5-dinitrophehalic anhydride with toluene.[156]

In reacting *m*-cresol with 4-nitrophthalic anhydride, two isomeric acids are obtained. Condensation is effected by gradually adding 20 g of aluminum chloride to a mixture of 10 g of the anhydride and 100 cc of the phenol, and subsequently heating, under stirring, for three to four hours at 130°. The products, 4-nitro-2-(2-hydroxy-4-methylbenzoyl)benzoic acid and the 5-nitro isomer, are separated by fractional crystallization from methyl alcohol and acetic acid.[157]

[152] A. Rieche and K. Jungholt, *Ber.*, 64, 578-589 (1931).
[154] W. A. Lawrance, *J. Am. Chem. Soc.*, 43, 2577-2581 (1921).
[155] P. C. Mitter and A. K. Sarkar, *J. Indian Chem. Soc.*, 7, 619-628 (1930); *C. Z.*, 1931 I, 3557.
[156] P. C. Mitter and R. Goswami, *J. Indian Chem. Soc.*, 8, 685-688 (1931); *Brit. Chem. Abs.-A*, 1430 (1931).
[157] P. C. Mitter and N. N. Chatterji, *J. Indian Chem. Soc.*, 8, 783-786 (1931); *C. A.*, 26, 3502; *C. Z.*, 1932 I, 2715.

3-Nitrophthalic anhydride with *m*-cresol and aluminum chloride in *sym*-tetrachloroethane heated for 1½ hours at 120-130° yields only 3-nitro-2-(2-hydroxy-4-methylbenzoyl)benzoic acid.[158]



Subsequently, it was reported [159] that better yields of the acid are obtained if an excess of *m*-cresol is used instead of an indifferent solvent, and if the use of any alkali is avoided, the yield of the above acid is practically theoretical. The same acid may also be prepared from 3-nitrophthalic acid, *m*-cresol, and aluminum chloride, but this method affords only a 40 per cent yield.

The condensation of 3,5-dinitrophthalic anhydride with *m*-cresol under like conditions yields only 3,5-dinitro-2-(2-hydroxy-4-methylbenzoyl)benzoic acid.[159]

Acetylaminophthalic Anhydrides.—Amino- keto-acids may be prepared by reacting acetylaminophthalic anhydrides with aromatic hydrocarbons or phenols and hydrolyzing the aroyl-*o*-acetylamino benzoic acids obtained. In the condensation of 3- or 4-acetylaminophthalic anhydride with benzene or toluene, two isomeric amino keto-acids are secured in each case.[160] From 6.8 g of 3-acetylaminophthalic anhydride and 9 g of aluminum chloride in 50 cc of benzene are obtained 51 per cent of 3-amino-2-benzoylbenzoic acid (m.p. 193-4°), a small amount of the 6,2-isomer (m.p. 159-160°), and 11 per cent of diphenyl-3-(or 6)-aminophthalide, m.p. 86-89°. The phthalide may also be obtained in 31 per cent yield when the anhydride, aluminum chloride, and benzene are heated for seven hours, treated with 10 cc of acetic anhydride, and heated for another seven hours.

4-Acetylaminophthalic anhydride with benzene and aluminum chloride yields 5-amino-2-benzoylbenzoic acid (m.p. 193-4°), and the 2,4-isomer (m.p. 195-6°).

Toluene with 3- and 4-acetylaminophthalic anhydrides analogously gives 3-(or 6)-acetylamino-2-(4-methylbenzoyl)benzoic acids and 4-(or 5)-acetylamino-2-(4-methylbenzoyl)benzoic acids, respectively. The acids from 3-acetylaminophthalic anhydride were separated into one melting at 256-7° (20 per cent yield) and another at 206° (40 per cent yield). The product from the 4-acetylamino anhydride consisted mainly of one acid (m.p. 135-6°), secured in 62 per cent yield, together with another product

[158] R. Eder and C. Widmer, *Helv. Chim. Acta*, 5, 3-17 (1922); *C. Z.*, 1922 I, 1031. Swiss P. 95,630, 95,614, and 95,947 (1921) to R. Eder; *C. Z.*, 1923 IV, 664
[159] R. Eder and C. Widmer, *Helv. Chim. Acta*, 6, 419-424; *C. Z.*, 1923 III, 51; *J. Chem. Soc. Abs.*, 124 (I), 688 (1923).
[160] W. A. Lawrance, *J. Am. Chem. Soc.*, 42, 1871-1879 (1920); *C. A.*, 15, 94; *ibid*, 43, 2577-2581 (1921); *C. A.*, 16, 1068.

Table 27.

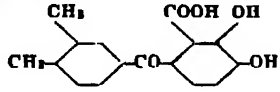
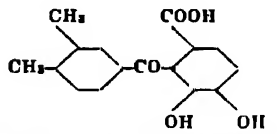
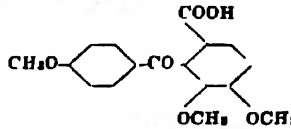
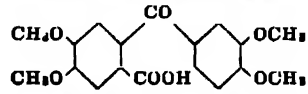
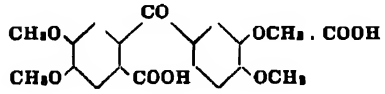
-Phthalic anhydride	Other reactant	-Benzoic acid	Solvent	Ref
4-methoxy	*o*-xylene	4-(or 5)-hydroxy-2-(3,3-dimethylbenzoyl)-, together with a product, m.p 134°	excess of xylene	5
4-methoxy	*p*-cresyl methyl ether	5-(or 4)-methoxy-2-(6-methoxy-3-methylbenzoyl)-	carbon disulfide	4
3-methoxy-4-methyl-	anisole	4-methyl-3-methoxy-2-(4-hydroxybenzoyl)-	excess of anisole	9
3,4-dimethoxy	benzene	6-hydroxy-5-methoxy- or 5-hydroxy-4-methoxy-2-benzoyl-	excess of benzene	7
3,4-dimethoxy	*o*-xylene	3,4- (or 5,6-)-dihydroxy-2-(3,4-dimethylbenzoyl)-  or 	excess of xylene	5
3,4-dimethoxy	*o*-cresol	3,4-dimethoxy-2-(2-hydroxy-3-methylbenzoyl)-	$CHCl_2CHCl_2$	9
3,4-dimethoxy	anisole	3,4-dimethoxy-2-anisoyl-  (1 g from 2 g anhydride and 3 g anisole)	benzene	6
3,4-dimethoxy	veratrole	5,6 (or 3,4)-dimethoxy-2-(3,4-dimethoxybenzoyl)-	CS_2	8
3,4-dimethoxy	pyrogallol trimethyl ether	hydroxy-tetramethoxy-2-benzoyl-	CS_2	8
3,5-dimethoxy	*m*-cresol	3,5-dimethoxy-2-(2-hydroxy-4-methylbenzoyl)- (45% yield) together with a phthalein	excess of cresol	3
3,5-dimethoxy-	*m*-cresyl methyl ether	3,5-dimethoxy-2-(4-methoxy-2-methylbenzoyl)- (40% yield) together with a phthalein		3
3,5-dimethoxy	6-nitro-*m*-cresol	3,5-dimethoxy-2(4-hydroxy-3-methyl-5-nitrobenzoyl)- (62% yield) and a trace of phthalein	excess of cresol	3
3,6-dimethoxy	*o*-cresol	3,6-dimethoxy-2-(3-hydroxy-2-methylbenzoyl)- (33% yield) together with a phthalein and a diphenylphthalide	excess of cresol	3
3,6-dimethoxy	*p*-cresol	3,6-dimethoxy-2-(3-hydroxy-6-methylbenzoyl)- (18% yield) together with a diphenyl phthalide and a fluoran	excess of cresol	3
3,6-dimethoxy	*m*-cresol	3,6-dimethoxy-2-(2-hydroxy-4-methylbenzoyl)- (50% yield); 3-hydroxy-6-methoxy isomer (small amount); a phthalein; and a diphenylphthalide	excess of cresol	3
3,6-dimethoxy	*o*-cresyl methyl ether	3,6-dimethoxy-2-(4-methoxy-5-methylbenzoyl)- (36% yield) and a diphenylphthalide (70% yield)	excess of the ether	2
3,6-dimethoxy	*o*-cresyl methyl ether	3,6-dimethoxy-2-(3-methyl-6-methoxybenzoyl)- (7 g from 20 g anhydride and 14 g ether)	carbon disulfide	1

Table 27—*(Continued)*

-Phthalic anhydride	Other reactant	-Benzoic acid	Solvent	Ref.
3,6-dimethoxy	*p*-cresyl methyl ether	3,6-dimethoxy-2-(2-methoxy-5-methylbenzoyl)- (44% yield) and a diphenylphthalide (21% yield)	excess of the ether	2
3,6-dimethoxy	*m*-cresyl methyl ether	3-hydroxy-6-methoxy-2-(4-methoxy-1-methylbenzoyl)- (65% yield)	excess of the ether	2
4,5-dimethoxy	veratrole	4,5-dimethoxy-2-(3,4-dimethoxybenzoyl)- 	CS_2	10
4,5-dimethoxy	resorcinol dimethyl ether	4,5-dimethoxy-2-(2-hydroxy-4-methoxybenzoyl)- ("satisfactory yield")		11
4,5-dimethoxy	ethyl-3-methoxy-phenoxy-acetate	brasilinic acid, 4,5-dimethoxy-2-[4-methoxy-2-(carboxymethoxy)-benzoyl]- 	CS_2	11

References

1. J. H. Cruickshank, H. Raistrick, and R Robinson, *J Chem. Soc*, 2056-2064 (1938); *C. A.*, 33, 1708.
2. J. H. Gardner and R Adams, *J Am Chem Soc*, 45, 2455-2462 (1923); *J. Chem Soc. Abs.*, 126 (I), 299 (1924)
3. G. D. Graves and R Adams, *J. Am. Chem Soc*, 45, 2439-2455 (1923), *J Chem. Soc. Abs*, 126 (I), 298 (1924).
4. W. H. Bentley, H D. Gardner, and C Weizmann, *J. Chem. Soc*, 91, 1626-1640 (1907).
5. H. Bradbury and C Weizmann, *J. Chem Soc*, 105, 2748-2751 (1914)
6. A. Bistrzycki and D. W Yssel de Schepper, *Ber*, 31, 2790-2802 (1898)
7. K. Lagodzinski, *Ber*, 28, 1427-1429 (1895)
8. W. H. Bentley and C Weizmann, *J Chem Soc*, 93, 435-438 (1908).
9. J L. Simonsen and M G Rau, *J Chem Soc*, 119, 1339-1348 (1921).
10. R D Haworth and C. R. Mavin, *J. Chem. Soc*, 1363-1366 (1931); *Brit. Chem. Abs*-A, 954 (1931).
11. W. H. Perkin and R. Robinson, *J. Chem. Soc*, 93, 489-517 (1908).

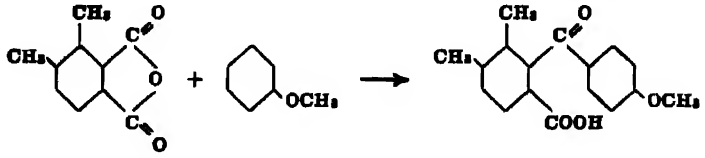
(m.p. 180-183°), probably its isomer, but obtained in too small a quantity to permit identification.

Methoxy Phthalic Anhydrides.—Condensations of methoxyphthalic anhydrides with aromatic hydrocarbons, phenols, and phenol ethers in the presence of aluminum chloride are listed in Table 27.

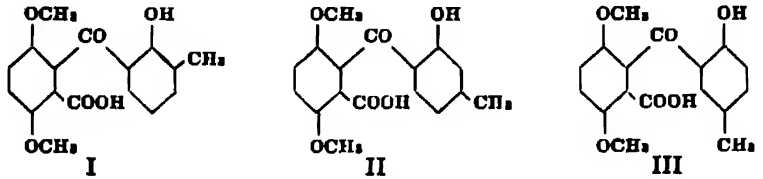
The Friedel-Crafts reaction of methoxyphthalic anhydrides has been investigated particularly with the object of preparing poly-hydroxyanthraquinones. For this reason, condensations of dimethoxy-phthalic anhydrides with phenols and phenol ethers have been primarily studied. In spite of the fact that efforts have been directed at the determination of the structure of the reaction products, inspection of Table 27 shows that there is ambiguity concerning the identity of some of the keto-acids prepared. In 1898, Bistrzycki and Yssel de Schepper [161] showed that reaction of 3,4-dimethoxyphthalic anhydride (hemipinic anhydride) with anisole and aluminum chloride in benzene solution gives 3,4-dimethoxy-2-anisoylbenzoic acid. It was shown definitely in this case that the carboxyl group in the *o*-position to the methoxy entered the reaction, and

[161] A. Bistrzycki and D. W. Yssel de Schepper, *Ber.*, 31, 2790-2802 (1898).

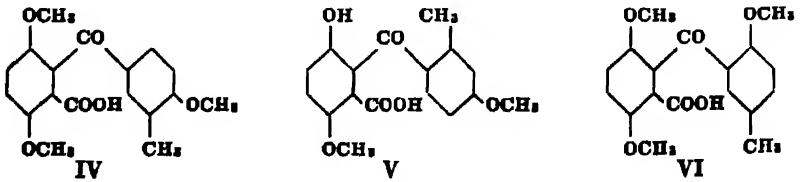
that condensation occurred with introduction of the anhydride residue at the carbon in *p*-position to the methoxy group of anisole:



More recently, in reactions effected with 3,6-dimethoxyphthalic anhydride and the three cresols, it has been shown that condensation occurs with the entering group taking the *o*-position to the hydroxy group of the cresols, and that keto-acids secured from *o*-, *m*-, and *p*-cresol had structures I, II, and III, respectively [162]:



In a similar study dealing with the condensation of cresyl methyl ethers with 3,6-dimethoxyphthalic anhydride, however, it was established that the entering group goes *para*- to the methoxyl group in the *o*- and *m*-cresyl methyl ethers, and to the *ortho*-position to the methoxyl in *p*-cresyl methyl ether.[163] The benzoylbenzoic acids derived from *o*-, *m*-, and *p*-cresyl methyl ethers have structures IV, V, and VI, respectively



Hydrolysis of a methoxy group in the reaction with *m*-cresyl methyl ether was due to the fact that the condensation was effected under unusually energetic conditions. Whereas in the reaction with the other ethers heating was effected for four or five hours at 65-70°, in the experiment with the *m*-isomer heating at 75° was maintained for seven hours.

A noteworthy condensation is that of *o*-nitro-*m*-cresol with 3,5-dimethoxyphthalic anhydride, in which a mixture of 10 g of the anhydride,

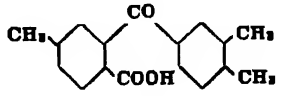
[162] G. D. Graves and R. Adams, *J. Am. Chem. Soc.*, 45, 2420-2435 (1923); *J. Chem. Soc. Abs.*, 126 (I), 288 (1924).
[163] J. H. Gardner and R. Adams, *J. Am. Chem. Soc.*, 45, 2435-2442 (1923); *J. Chem. Soc. Abs.*, 126 (I), 289 (1924).

35 g of the cresol, and 20 g of aluminum chloride, heated for 20 hours at 75° gave a 62 per cent yield of 3,5-dimethoxy-2-(4-hydroxy-2-methyl-5-nitrobenzoyl)benzoic acid. This is one of the few instances in which a nitrophenol has been reported to undergo Friedel-Crafts reaction.

Solvents used in reactions with methoxyphthalic anhydrides have been listed in Table 27. Although Ullmann and Schmidt[164] have obtained excellent results by using *sym*-tetrachloroethane as solvent in condensations of other phthalic anhydrides with phenols and aluminum chloride, their method could not be used in reactions involving 3,6-dimethoxyphthalic anhydride and cresols because decomposition of the anhydride occurred.[162] The use of *sym*-tetrachloroethane as solvent is reported in the reaction of the 3,4-dimethoxy anhydride and *o*-cresol, but the yield of the resulting keto-acid is not given.[165]

Alkyl Phthalic Anhydrides.—Condensations of methylphthalic anhydrides with aromatic hydrocarbons and phenols in the presence of aluminum chloride have been studied by only a few workers; since the researches of each investigator have been very thorough the individual studies will be separately reviewed.

In 1929, Morgan and Coulson[166] reported the condensation of 4-methylphthalic anhydride with toluene. Reaction was effected by adding 15 g of aluminum chloride to 9 g of the anhydride in 40 g of toluene and heating until evolution of hydrogen chloride had ceased. Only 1 g of the expected keto-acid, 4-methyl-2-(4-methylbenzoyl)benzoic acid was secured. In an analogous reaction with *o*-xylene instead of toluene, the addition of 7 g of aluminum chloride to a paste consisting of 4 g of the anhydride and 21 g of *o*-xylene gave, after heating at 90-100° until evolution of hydrogen chloride had ceased, a dark, gummy product from which was secured 3 g of 4-methyl-2-(3,4-dimethylbenzoyl)benzoic acid:



A series of condensations with methylated phthalic anhydrides has been investigated by Mayer and Stark.[167] Their investigations are summarized on p. 556.

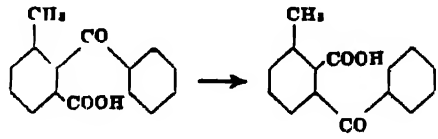
A great deal of work has also been done by Hayashi and co-workers on condensations effected with 3- and 4-methylphthalic anhydrides. Reactions with benzene were effected in excess of the hydrocarbons; *sym*-tetrachloroethane was used as solvent in condensations with phenols. The products are usually mixtures of isomeric keto-acids which, in the early work of these investigators, could not be identified through ring-closure

[164] F. Ullmann and W. Schmidt, *Ber.*, 52, 2098-2115 (1919).
[165] J. L. Simonsen and M. G. Rau, *J. Chem. Soc.*, 119, 1338-1345 (1921).
[166] G. T. Morgan and E. A. Coulson, *J. Chem. Soc.*, 2551-2559 (1929).
[167] F. Mayer and O. Stark, *Ber.*, 64, 2008-2010 (1931); *Brit. Chem. Abs.*-A, 1296 (1931).

Condensations with Methylated Phthalic Anhydrides.[167]

-Phthalic anhydride	Other Reactant	Conditions	Product
3-methyl	benzene	reaction mixture stirred for 2 days and heated at 50° for 2 hours, excess of benzene	a 70% yield of a mixture of 6- and 3-methyl-2-benzoylbenzoic acids
3-methyl	toluene	excess of toluene	a mixture of 6- and 3-methyl-2-(4'-methylbenzoyl)-benzoic acids
3-methyl	*p*-xylene	CS_2 solution	a 77% yield of a mixture of 3- and 6-methyl-2-(2',5'-dimethylbenzoyl)-benzoic acids
3-methyl	hydroquinone	$AlCl_3$-NaCl melt at 180° for one hour	58% yield of 1-methyl-5,8-dihydroxyanthraquinone
3-methyl	hydroquinone	$AlCl_3$-NaCl melt at 180° for 20 minutes	3- or 6-methyl-2-(2',5'-dihydroxybenzoyl)-benzoic acids
3-methyl	toluhydroquinone	$AlCl_3$-NaCl melt at 160-190°	1,7- or 1,6-dimethyl-5,8-dihydroxyanthraquinone
3-methyl	hydroxyhydroquinone	as above	30% yield of 1-methyl-5,6,8- or 5,7,8-trihydroxyanthraquinone
3-methyl	resorcinol	as above	1-methyl-5,7-dihydroxyanthraquinone
3-methyl	pyrocatechol	as above	1-methyl-5,6-dihydroxy- or 1-methyl-7,8-dihydroxyanthraquinone
4-methyl	*p*-xylene	excess of *p*-xylene	4- or 5-methyl-2-(2',5'-dimethylbenzoyl)-benzoic acid
4-methyl	*m*-xylene	CS_2 solution, reaction mixture allowed to stand for 6 days at	61% yield of a mixture of 3- and 5-methyl-2-(2',4'-dimethylbenzoyl) benzoic acids
3,6-dimethyl	toluene		3,6-dimethyl-2-(4'-methylbenzoyl)-benzoic acid
3,6-dimethyl	hydroquinone	$AlCl_3$-NaCl melt at 190°	1,4-dimethyl 5,8-dihydroxyanthraquinone
3,6-dimethyl	toluhydroquinone	at 185°	1,4,7-trimethyl-5,8-trihydroxyanthraquinone
3,6-dimethyl	hydroxyhydroquinone	at 180°	1,4-dimethyl-5,7,8-trihydroxyanthraquinone
3,6-dimethyl	pyrogallol	at 175°	1,4-dimethyl-5,6,7-trihydroxyanthraquinone

by sulfuric acid In a paper [168] which summ
vious studies of these investigators, the assumption that benzoylbenzoic acids are rearranged upon heating with sulfuric acid was definitely proved. Thus, upon heating 3-methyl-2-benzoylbenzoic acid with sulfuric acid at 100-105°, an isomerism occurs, possibly because of a wandering of the benzoyl group, and 6-methyl-2-benzoylbenzoic acid is secured



Other conversions of this type showed that 3- and 6-methyl-2-benzoylbenzoic acids exist in equilibrium with sulfuric acids. On this basis, ketoacids given tentative and optional structures in earlier work were definitely characterized. The investigations of Hayashi and his co-workers are summarized:

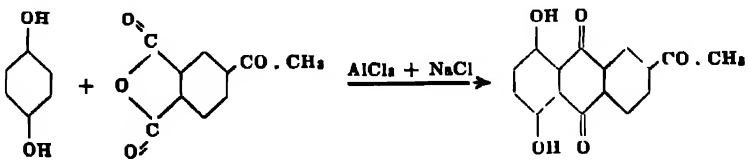
[168] M. Hayashi, S. Tsuruoka, I Morikawa, and H. Namikawa, *Bull. Chem Soc. Japan*, 11, 184 200 (1936); *C. A.*, 30, 3985.

-Methyl phthalic anhydride	Other reactant	-benzoic Acid	m.p. (°C)	Ref.
4-	benzene	{2-benzoyl-4-methyl- 2-benzoyl-5-methyl-	150-150.5 145-145.5	2, 6
4-	*p*-chlorophenol	2-(5'-chloro-2'-hydroxybenzoyl)-4-methyl- 2-(5'-chloro-2'-hydroxybenzoyl)-5-methyl-	239.5-240.5 227.5-228.5	2, 6
3-	benzene	{6-methyl-2-benzoyl- 3-methyl-2-benzoyl-	126.5-127.5 171-172	6, 5
3-	chlorobenzene	2-(4'-chlorobenzoyl)-3-methyl-	175.5-176	6, 5
3-	phenol	{2-(2'-hydroxybenzoyl)-3-methyl- 2-(4'-hydroxybenzoyl)-3-methyl-	220-221 197-198	6, 5
3-	*o*-chlorophenol or *o*-chloroanisole	2-(3'-chloro-4'-hydroxybenzoyl)-3-methyl-	198-199	3, 5
3-	*p*-bromophenol	2-(5'-bromo-2'-hydroxybenzoyl)-3-methyl-	246-246.5	1, 6
3-	*p*-chlorophenol or *p*-chloroanisole	2-(5'-chloro-2'-hydroxybenzoyl)-3-methyl-	238-239	1, 6
3-	*m*-chlorophenol or *m*-chloroanisole	{2-(4'-chloro-2'-hydroxybenzoyl)-3-methyl- 2-(2'-chloro-4'-hydroxybenzoyl)-3-methyl-	219.5-220.5 218-218.5	4, 6
3-	hydroquinone	2-(2',5'-dihydroxybenzoyl)-3 (or 6)-methyl-	232.5-233	4

References

1. M. Hayashi, *J. Chem. Soc.*, 2516-2527 (1927); *C. Z.*, 1928 I, 346.
2. M. Hayashi, *J. Chem. Soc.*, 1513-1519 (1930); *C. Z.*, 1930 II, 1697.
3. M. Hayashi, *J. Chem. Soc.*, 1520-1523 (1930); *C. Z.*, 1930 II, 1698.
4. M. Hayashi, *J. Chem. Soc.*, 1524-1528 (1930); *C. Z.*, 1930 II, 1699.
5. M. Hayashi and S. Tsuruoka, *J. Chem. Soc. Japan*, 56, 1031-1034 (1935); *C. A.*, 30, 1046.
6. M. Hayashi, S. Tsuruoka, I. Morikawa and H. Namikawa, *Bull. Chem. Soc. Japan*, 11, 184-200 (1936); *C. Z.*, 1936 II, 1719; *C. A.*, 30, 5965

Keto-Phthalic Anhydrides. - A few investigators cite the use of acylated phthalic anhydrides in Friedel-Crafts reactions. 4-Acetylphthalic anhydride has been condensed with hydroquinone using a melt of $AlCl_3$-NaCl at 180° for 45 minutes to produce 5,8-dihydroxy-2-acetylanthraquinone. From 4 g each of the anhydride and hydroquinone, there is secured 4.7 g of the anthraquinone derivative:



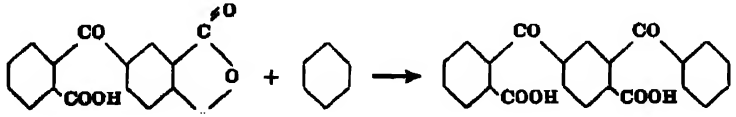
Like treatment of toluhydroquinone instead of hydroquinone produced 2-acetyl-6 (or 7)-methyl-5,8-dihydroxyanthraquinone, and analogous reaction with 1,4-naphthohydroquinone yields 7 g of 2-acetyl-5,8-dihydroxy-6,7-benzoanthraquinone.[189]

The condensation of acetylamino- derivatives with aromatic compounds and aluminum chloride has already been mentioned (pp. 257, 551).

The Friedel-Crafts reaction has also been applied to condensations effected with 4-(2-carboxybenzoyl)phthalic anhydride. Treatment of

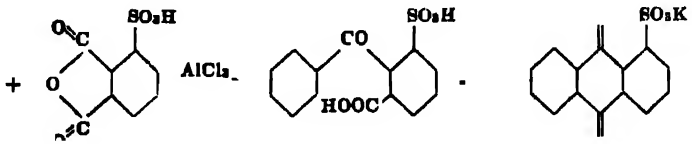
[189] F. Mayer, O. Stark, and K. Schön, *Ber.*, 65, 1533-1537 (1932).

the latter with benzene and aluminum chloride yields 1,5-dibenzoylbenzene-2,2'-dicarboxylic acid [170]:

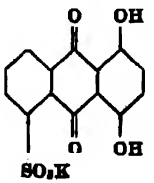


Toluene reacts analogously.[171]

Sulfophthalic Anhydrides.—Sulfonated anthraquinones may be formed by reaction of sulfophthalic anhydride with aromatic hydrocarbons or their halogenated derivatives in the presence of aluminum chloride.[172] Upon heating 3-sulfophthalic anhydride with benzene and aluminum chloride at 130°, converting the resulting benzoylsulfobenzoic acid to its potassium salt and heating it at 160°, and further treating with 5 per cent oleum, the potassium salt of anthraquinone-1-sulfonic acid is secured in 70 per cent yield.



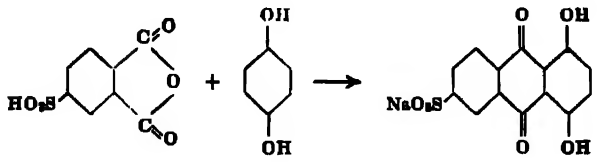
Analogously, *p*-dichlorobenzene yields potassium 1,4-dichloroanthraquinone-5-sulfonate in 40 per cent yield, and hydroquinone gives potassium 1,4-dihydroxyanthraquinone-5-sulfonate.



Condensation of 4-sulfophthalic anhydride with benzene, and the formation of the sodium salt of anthraquinone-2-sulfonic acid proceeds readily, a very good yield of the latter being secured. With chlorobenzene two isomeric keto-acids, 2- and 3-chloroanthraquinone-6-sulfonic acids, are obtained. That 4-sulfophthalic anhydride is very reactive may be surmised from the fact that with the ordinarily difficultly substituted *p*-dichlorobenzene, sodium 1,4-dichloroanthraquinone-6-sulfonate, resulting upon ring closure of the intermediately formed keto-acid, is obtained

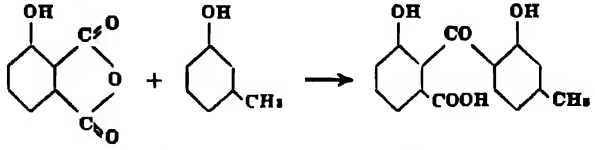
[170] H. de Diesbach and L. Chardonnens, *Helv. Chim. Acta*, 7, 809-813 (1924); *J. Chem. Soc. Abs.*, 126 (I), 1061 (1924).
[171] H. Limpricht, *Ann.*, 312, 99-109 (1900); *J. Chem. Soc. Abs.*, 78 (I), 898 (1900).
[172] E. Schwenk and H. Waldmann, *Z. angew. Chem.* 45, 17-21 (1932); *C. Z.*, 1932 I, 1871.

in 60 per cent yield. With hydroquinone like reaction leads to a 70 per cent yield of sodium 1,4-dihydroxyanthraquinone-6-sulfonate:



This method of preparing anthraquinone sulfonic acid has been stated to be more effective than that involving sulfonation of anthraquinones with oleum, since the latter procedure often results in the simultaneous formation of disulfonic acids.

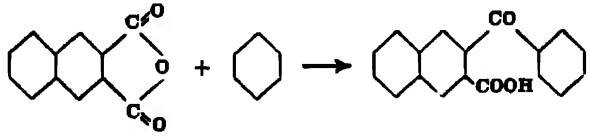
Hydroxyphthalic Anhydrides.—Although little work has been done on Friedel-Crafts reactions with hydroxy- derivatives of phthalic anhydride, it has been reported that 3-hydroxyphthalic anhydride condenses with *m*-cresol in the presence of aluminum chloride to give a comparatively poor yield of 2′-hydroxy-4′-methyl-2-benzoyl-3-hydroxybenzoic acid [173]:



Aromatic Dicarboxylic Acid Anhydrides other than Phthalic Anhydrides

Naphthalene Dicarboxylic Acid Anhydrides.—The anhydrides of naphthalene-*o*-dicarboxylic acids behave in Friedel-Crafts reactions very much as does phthalic anhydride.

Reactions of naphthalene-2,3-dicarboxylic anhydride with aromatic hydrocarbons and phenols have been extensively studied by Waldmann and Mathiowetz.[174] With benzene, condensation occurs upon heating in the presence of aluminum chloride for eight hours at 120° with formation of 2-benzoyl-3-naphthoic acid in 87 per cent yield:

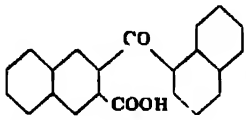


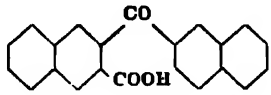
Reaction with toluene takes place analogously, yielding 2-(*p*-methylbenzoyl)-3-naphthoic acid. In the condensation with chlorobenzene heating is maintained for eight hours at 100°. From 30 g of the anhy-

[173] R. Eder and C. Widmer, *Helv. Chim. Acta*, **6**, 419-434 (1923).
[174] H. Waldemann and H. Mathiowetz, *Ber.*, **64**, 1713-1724 (1931).

dride and 145 g of chlorobenzene, with 50 g of aluminum chloride there is secured 31 g of 2-(*p*-chlorobenzoyl)-3-naphthoic acid.

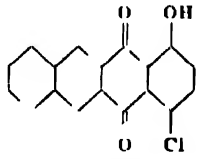
Addition of naphthalene-2,3-dicarboxylic anhydride to naphthalene was effected by heating to boiling for 48 hours a mixture consisting of 33 g of the anhydride, 32.5 g of naphthalene and 58 g of aluminum chloride in 75 cc of carbon disulfide. There was secured 28 g of a mixture of isomeric naphthoylnaphthoic acids:



and


An $AlCl_3$-NaCl melt was used in the reaction of phenols with naphthalene-2,3-dicarboxylic acid anhydride. These condensations are summarized:

Table 28.

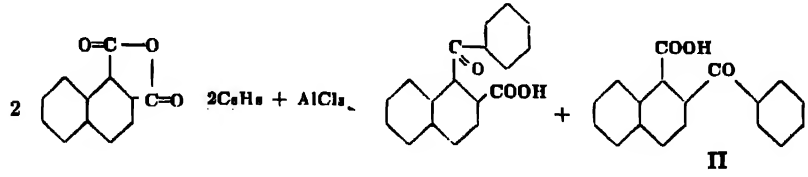
Phenol	Conditions	Products
p-Chlorophenol	3 hrs at 210°	1-chloro-4-hydroxy-2,3-benzanthraquinone (22 g from 20 g anhydride and 14.2 g of the phenol) 
p-Cresol		1-methyl-4-hydroxy-2,3-benzanthraquinone
Hydroquinone	3 hrs. at 200-210°	1,4-dihydroxy-2,3-benzanthraquinone (65% yield)
2-Chlorohydroquinone	1 hr. at 200-210°	2-chloro-1,4-dihydroxy-2,3-benzanthraquinone (61% yield)
Methylhydroquinone		2-methyl-1,4-dihydroxy-2,3-benzanthraquinone
2-Hydroxyhydroquinone		1,2,4-trihydroxy-2,3-benzanthraquinone
α-Naphthol	30 mins at 220°	9-hydroxy-2,3,6,7-dibenzanthraquinone
1,4-Dihydroxynaphthalene		9,10-dihydroxy-2,3,6,7-dibenzanthraquinone

The condensation of dihydroquinizarin with naphthalene-2,3-dicarboxylic acid anhydride at elevated temperatures with 5 per cent aluminum chloride has been reported by Marschalk [175] to result in the formation of a hexacene derivative.

The reaction of 1-phenyl-2,3-naphthalic anhydride in benzene with aluminum chloride gives a 99 per cent yield of 3,4-benzo-9-fluorenone-1-carboxylic acid. Here, instead of addition of the anhydride with benzene, an intramolecular condensation occurs.[176]

[175] C. Marschalk, *Bull. soc. chim. (5)*, **5**, 806-809 (1938); *C. A.*, **[illegible]**, 4574.
[176] L. F. Fieser and L. M. Joshel, *J. Am. Chem. Soc.*, **62**, 957-9[illegible] (1940); *cf.* M. Schnarschmidt and N. Irineu, *Ber.*, **48**, 1826-1832 (1915).

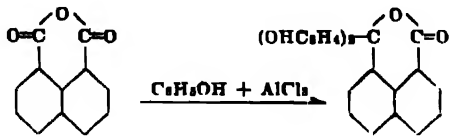
The interaction of naphthalene-1,2-dicarboxylic acid anhydride with aromatic hydrocarbons, their halogen derivatives, and phenols has been investigated by Waldmann.[177] At first it was believed that only one keto-acid was obtained; the reaction with benzene was reported to yield 1-benzoyl-2-naphthoic acid and that with chlorobenzene, 1-*p*-chlorobenzoyl-2-naphthoic acid. In his later work, however, Waldmann found that naphthalene-1,2-dicarboxylic anhydride yielded two isomeric acids when reacted with benzene and aluminum chloride. Besides 1-benzoyl-2-naphthoic acid (I) there was also isolated 2-benzoyl-1-naphthoic acid (II).



Using a 5:1 $AlCl_3$-NaCl melt and heating for three hours at 200-210°, hydroxybenzanthraquinones were secured by reaction of the anhydride with various phenols. Hydroquinone and 1,4-dihydroxynaphthalenes afford only one product; in all other cases listed below 2 isomeric benzanthraquinones are possible, but they could not be differentiated in the reaction product.

Phenol	-benzanthraquinones obtained
Hydroquinone	5,8-dihydroxy-1,2-
Toluhydroquinone	6-(7)-methyl-5,8-dihydroxy-1,2-
Chlorohydroquinone	6-(7)-chloro-5,8-dihydroxy-1,2-
Hydroxyhydroquinone	5,6-(7),8-trihydroxy-1,2-
p-Chlorophenol	5-(8)-chloro-8-(5)-hydroxy-1,2-
p-Cresol	5-(8)-methyl-8-(5)-hydroxy-1,2-
1,4-Dihydroxynaphthalene	5,8-dihydroxy-1,2,6,7-di-
α-Naphthol	5-(8)-hydroxy-1,2,6,7-di-

The condensation of naphthalene-1,8-dicarboxylic acid anhydride (naphthalic anhydride) with phenol and aluminum chloride has been reported to yield phenolnaphthalein:



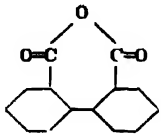
Reaction was effected by heating 20 g of the naphthalic anhydride, 80 g of phenol, and 50 g of aluminum chloride at 160° until evolution of hydrogen chloride had ceased.[178]

[177] H. Waldmann, *J. prakt. Chem. (2)*, 127, 193-200 (1930); *C. A.*, 24, 5743; *J. prakt. Chem. (2)*, 131, 71-81 (1931); *C. Z.*, 1931 II, 2010.
[178] G. F. Jaubert, *Ber.*, 28, 991-994 (1895).

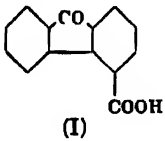
Naphthalic anhydride reacts with dimethyl-*m*-aminophenol in the presence of aluminum chloride to give a compound (m.p. 320°) which is practically identical in color with Rhodamine.[179]

Attempts to condense benzene with naphthalic anhydride in the presence of aluminum chloride have been unsuccessful, the anhydride being recovered unchanged each time.[180]

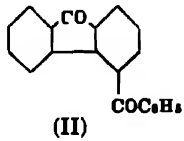
Biphenic Anhydride.—Contradictory results have been secured in Friedel-Crafts reactions with biphenic anhydride,



Götz [181] reported that on boiling a solution of biphenic anhydride in benzene with excess of aluminum chloride, there is produced a 50 per cent yield of fluorenone-4-carboxylic acid (I) and a 10-15 per cent yield of 4-benzoylfluorenone (II):



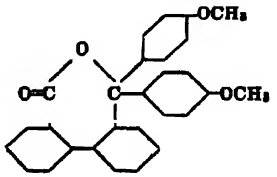
(I)



(II)

Fluorenone-4-carboxylic acid, together with 4-*p*-toluylfluorenone, was also reported to be obtained by condensation of biphenic anhydride with toluene and aluminum chloride.[182]

More recently, Underwood and Barker [183] reacted 5 g of biphenic anhydride with 3.5 g of anisole and 3 1 g of aluminum chloride and secured an 11 per cent yield of the crystalline lactone, the dimethyl ether of phenoldiphenein:



From a comprehensive study of the reaction of biphenic anhydride with phenols and hydrocarbon, Bell and Briggs [184] concluded that in spite

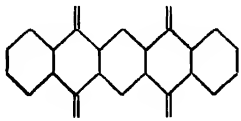
[179] E. Ferrario and L. F. Weber, *Arch. sci. phys. nat.*, 25, 517-518 (1908); *C. A.*, 2, 2382.
[180] O. R. Quayle and E. E. Reid, *J. Am Chem. Soc.*, 47, 2357-2361 (1925).
[181] R. Götz, *Monatsh.*, 23, 27-43 (1902); *J. Chem. Soc. Abs*, 82 (I), 873 (1902).
[182] H. Pick, *Monatsh.*, 25, 979-989 (1904); *J. Chem. Soc. Abs.*, 86 (I), 68 (1906).
[183] H. W. Underwood, Jr., and G. E. Barker, *J Am. Chem. Soc.*, 52, 4052-4057 (1930).
[184] F. Bell and F. Briggs, *J. Chem. Soc.*, 1561-1568 (1933).

of statements to the contrary in the literature, evidence for the production of compounds analogous to phenolphthalein and fluorescein is lacking. These investigators report that treatment of hydrocarbons with biphenic anhydride in the presence of aluminum chloride gave the following results: benzene, toluene, and ethylbenzene underwent no reaction; the biphenic anhydride was recovered as diphenic acid and as fluorenone-4-carboxylic acid; biphenyl gave non-crystallizable material; *o*-, *m*-, and *p*-xylenes, mesitylene, and naphthalene gave derivatives of 2-benzoylbiphenyl-2′-carboxylic acid; *p*-xylene in addition yielded 2,2′-bis-(2″,5″-dimethylbenzoyl)biphenyl; naphthalene gave 2-naphthoylbiphenyl-2′-carboxylic acid; anisole yielded a small amount of 2-anisoylbiphenyl-2′-carboxylic acid, fluorenone-4-carboxylic acid, and 4-anisoylfluorenone. On the other hand, phenetole gave a good yield of the only product isolated, 2-(*p*-ethoxybenzoyl)biphenyl-2′-carboxylic acid.

The condensation of biphenic anhydride with phenols was studied also in the presence of stannic chloride. In most cases there was obtained a mixture of the corresponding diketone and a ketonic carboxylic acid.

Anthracene Dicarboxylic Acid Anhydrides.—Friedel-Crafts condensations with anthraquinone dicarboxylic anhydrides have been studied with the object of preparing pentacene and hexacene derivatives through ring closure of primarily formed keto-acids.

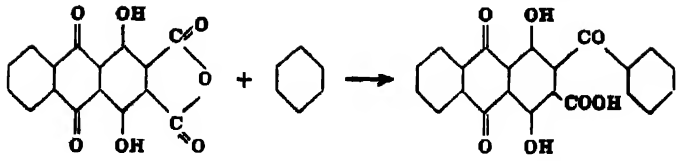
Condensation of anthraquinone-2,3-dicarboxylic acid anhydride with benzene and aluminum chloride and subsequent ring closure with sulfuric acid has been reported[185] to proceed with formation of *lin*-dibenzo-1,4,5,8-anthradiquinone:



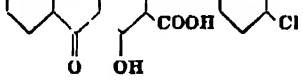
Anthraquinone-2,3-dicarboxylic acid anhydride has been condensed with hydroquinone in the presence of aluminum chloride to give a substance which is believed to be 6,7-phthaloylquinizarin.[186] Reactions of this anhydride with dihydroquinizarin gave a supposed octacene derivtive. A similar product was obtained by condensation of anthracene-2,3-dicarboxylic acid anhydride and dihydroxy-1,4-dihydronaphthacenequinone.

1,4-Dihydroxyanthraquinone-2,3-dicarboxylic acid anhydride reacts normally with benzene and aluminum chloride to give 1,4-dihydroxy-2-benzoylanthraquinone-3-carboxylic acid[187]:

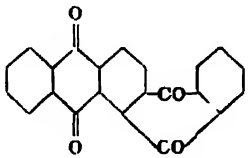
[185] A. Fairbourne, *J. Chem. Soc.*, 119, 1573-1582 (1921); *C. Z.*, 1922 I, 564.
[186] C. Marschalk, *Bull. soc. chim. (5)*, 5, 306-309 (1938); *C. A.*, 32, 4574.
[187] C. Marschalk, *Bull. soc. chim. (5)*, 3, 2155-2158 (1936); *C. A.*, 31, 8525 (1937).



By agitating a suspension of 20 g of the finely divided anhydride in 200 g of anhydrous benzene in the presence of 40 g of aluminum chloride for thirty minutes, refluxing for six hours, decomposing with iced hydrochloric acid, steam distilling, boiling the residue with sodium carbonate, filtering, washing with water and recrystallizing from nitrobenzene and then xylene, 16 g of the above keto-acid was secured.[188] Using the same procedure, except that heating was maintained for six hours at 45-50°, 10.7 g of 1,4-dihydroxy-2-*p*-toluylanthraquinone-3-carboxylic acid was obtained when toluene was substituted for the benzene. Replacement of the benzene with chlorobenzene, and conducting the reaction for 21 hours at 65-70°, gives 16-18 g of 1,4-dihydroxy-2-(4-chlorobenzoyl) anthraquinone-3-carboxylic acid.



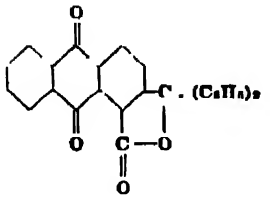
According to Fairbourne[185] the reaction of anthraquinone-1,2-dicarboxylic acid anhydride with benzene and aluminum chloride followed by cyclization with sulfuric acid yields 1,2-phthalylanthraquinone,



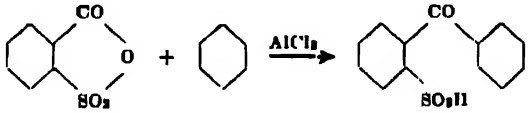
Reaction was effected by cautiously heating, until evolution of hydrogen chloride had ceased, a mixture consisting of 10 g of the anhydride and 10 g of aluminum chloride in 1 liter of benzene.

Machek and Graf,[189] however, state that the product obtained by Fairbourne cannot be 1,2-phthalylanthraquinone because it does not agree in physical properties with it. These investigators heated to boiling for two hours a mixture of 2 g of anthraquinone-1,2-dicarboxylic anhydride, 60 g of benzene, and 6 g of aluminum chloride and secured the phthalide, m. 180-182°:

[188] C. Marschalk, *Bull. soc. chim.* (5), 4, 184-186 (1937), *C. A.*, 31, 2040
[189] G. Machek and A. Graf, *Monatsh.*, 50, 6-9 (1928); *C. Z.*, 1928 II, 1328

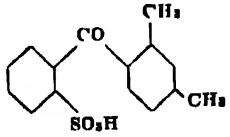


Sulfobenzoic Acid Anhydride.—Friedel-Crafts reaction of *o*-sulfobenzoic acid anhydride and aromatic hydrocarbons proceeds as does the like reaction with phthalic anhydride. Here, however, the product is a keto-sulfonic acid instead of a keto-carboxylic acid. With benzene, 2-benzoylbenzenesulfonic acid is secured:

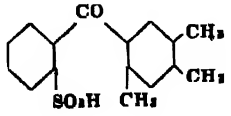


Condensation is effected by adding, in the cold, 20 g of aluminum chloride to a solution of 10 g of the acid in 50 g of benzene. Upon heating for one hour on a water-bath, the reaction mixture becomes a homogeneous liquid, from which the sulfonic acid is not precipitated upon decomposition with ice water. For this reaction the catalyst is removed by treatment with ammonia, and the sulfonic acid is secured as its ammonium salt, in a 90 per cent of theoretical yield. The free acid was obtained through its barium salt.

Analogous condensation with toluene yields 2-(4-methylbenzoyl) benzenesulfonic acid, and with *m*-xylene there is obtained what is probably 2-(2,4-dimethylbenzoyl)benzenesulfonic acid.

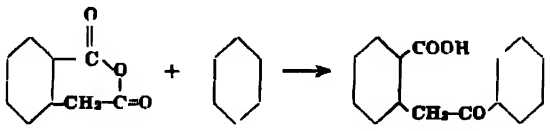


The reactions with benzene, toluene, and *m*-xylene were always accompanied by strong evolution of hydrogen chloride. When pseudocumene was reacted in analogous manner, however, no evolution of hydrogen chloride was noticed, although the product obtained was the expected keto-acid, 2-(3,4,6-trimethylbenzoyl)benzenesulfonic acid,

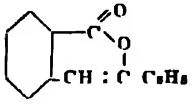


Hydrogen chloride evolution was again pronounced in the condensation with mesitylene, with formation of the corresponding compound, 2-(2,4,6-trimethylbenzoyl)benzenesulfonic acid.[190]

Homophthalic Anhydride.—The condensation of benzene with homophthalic anhydride and aluminum chloride results in introduction of the phenyl residue at the carbonyl of the aliphatic side chain,



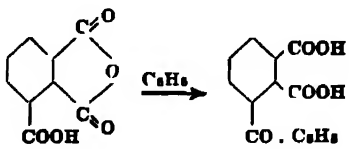
with formation of β-desoxybenzoincarboxylic acid.[191] A small amount of isobenzalphthalide,



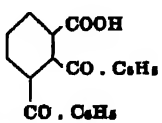
is also produced in the reaction.

Anhydrides of Aromatic Tricarboxylic Acids

Friedel-Crafts reaction with hemimellitic anhydride has been studied by Graebe and Leonhardt,[192] who found that the course of the condensation with benzene is greatly influenced by reaction time. If the finely powdered anhydride is mixed with 1-1.5 parts of aluminum chloride and 4-5 parts of benzene in the cold, and then heated under reflux for 20 to 25 minutes, or only until violent reaction has subsided, the product is benzoylphthalic acid:

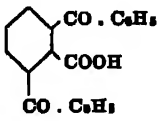


However, if heating is continued under reflux for five or six hours, the product is 2,3-dibenzoylbenzoic acid,

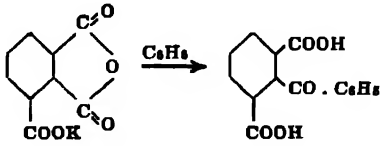


[190] C. Kranzlah, *Ber.*, **53**, 2485-2494 (1920).
[191] C. Graebe and F. Trümpy, *Ber.*, **31**, 375-377 (1898). cf. Buu-Hoi, *Compt. rend.*, **209**, 562-4 (1939); *C. A.*, **34**, 4783.
[192] C. Graebe and M. Leonhardt, *Ann.*, **290**, 217-238 (1896).

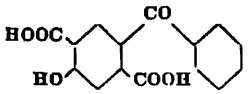
A shorter reaction period is favorable to the formation of 2,6-dibenzoylbenzoic acid,



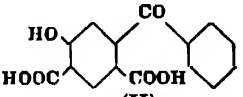
When the monopotassium salt of hemimellitic anhydride is used in the reaction with benzene and aluminum chloride, and heating is maintained for 20 to 25 minutes, the product is benzoylisophthalic acid:



Friedel-Crafts condensations of hydroxytrimellitic acid anhydride with aromatic hydrocarbons or phenols leads to the production of *o*-hydroxycarboxylic acids of the anthraquinone series.[193] When the anhydride is reacted with benzene at 80-100° in an $AlCl_3$-NaCl melt, there is obtained a substance (m.p. 259°) which is either 2-benzoyl-5-hydroxybenzene-1,4-dicarboxylic acid (I) or 2-benzoyl-4-hydroxybenzene-1,5-dicarboxylic acid (II), or a mixture of these compounds:

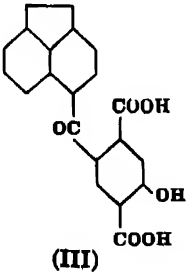


(I)

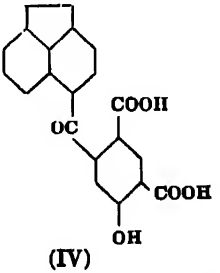


(II)

Toluene yields in the same way a product (m.p. 260°) which is either 2-(4'-methylbenzoyl)-5-hydroxybenzene-1,4-dicarboxylic acid or 2-(4'-methylbenzoyl)-4-hydroxybenzene-1,5 dicarboxylic acid, or their mixture. From hydroxytrimellitic anhydride and acenaphthene is secured under like conditions either 4'-hydroxy-2',5'-dicarboxy-5-benzoylacenaphthene (III) or 5'-hydroxy-2',4'-dicarboxy-5-benzoylacenaphthene (IV), or both:



(III)



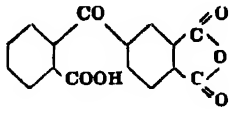
(IV)

[193] German P. II, 3464. (1933) to W. Eckert and K. Schilling (to I. G.); *C. A.*, 32, 6879; *C. Z.*, 1938

Like condensations also take place with hydroxytrimellitic anhydride and hydroquinone, 1,4-dihydroxynaphthalene, 1,4-dichlorobenzene, or hydroxyhydroquinone.

Halotrimellitic anhydride has been claimed to undergo a similar series of condensations.[194]

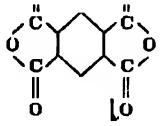
Friedel-Crafts reactions with 4-(2-carboxybenzoyl)phthalic anhydride,



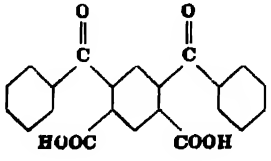
which may also be considered as an anhydride of a tricarboxylic acid, have been mentioned in the discussion of condensations effected with ketonic phthalic anhydrides (see p. 557).

Anhydrides of Aromatic Tetracarboxylic Acids

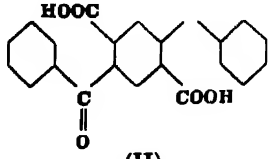
The anhydride of this type which has been most investigated is pyromellitic anhydride (the anhydride of benzene-1,2,4,5-tetracarboxylic acid):



It would be expected that Friedel-Crafts condensation of benzene would proceed with formation of either 4,6-dibenzoylisophthalic acid (I) or 2,5-dibenzoylterephthalic acid (II):



(I)



(II)

Philippi [195] has secured both isomers, and these were separated by making use of their solubility in water and nitrobenzene. Mills and Mills [196] likewise secured both isomers, obtaining a 60 per cent yield of

[194] French P. 831,646 (1937) to I. G.; *C. A.*, 32, 1771.
[195] E. Philippi, *Monatsh.*, 32, 631-634 (1911); *J. Chem. Soc. Abs.*, 100 (I), 708 (1911).
[196] W. H. Mills and M. Mills, *J. Chem. Soc.*, 101, 2194-2208 (1912).

the mixture of acids by heating for three hours at 65-70° a suspension of 30 g of finely ground pyromellitic anhydride in 750 cc of benzene with 70 g of aluminum chloride.

Bromobenzene reacts in an analogous manner, according to Philippi and Auslaender,[197] to form a mixture of 2,5-bis(*p*-bromobenzoyl)terephthalic acid and 4,6-bis-(*p*-bromobenzoyl)isophthalic acid; but Machek and Martin [198] believed that some cleavage of bromine was encountered, with the formation of the 2,5-dibenzoyl derivative, since cyclization of the products produced pentacene-5,7,12,14-diquinone as well as the expected product, 2,9-dibromopentacene-5,7,12,14-diquinone.

Pyromellitic anhydride with toluene and aluminum chloride forms mainly 4,6-bis(*p*-toluyl)isophthalic acid together with 2,5-bis(*p*-toluyl) terephthalic acid.[199] There is no indication of any further condensation reactions;[200] *o*- and *p*-xylene with pyromellitic anhydride also produce the two isomeric acids. *p*-Xylene gives a mixture of 4,6-bis(*p*-xyloyl)-isophthalic- and 2,5-bis(*p*-xyloyl)terephthalic acids.[201] From *o*-xylene there are secured 4,6-bis(3,4-dimethylbenzoyl)isophthalic- and 2,5-bis-(3,4-dimethylbenzoyl)terephthalic acids.[202]

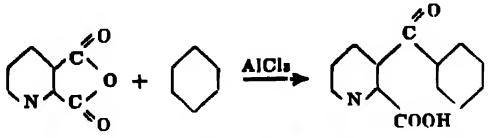
When aluminum chloride is added to a mixture of pyromellitic anhydride, naphthalene, and benzene and heated at 30-60° for ten hours, 4,6-di-α-naphthoylisophthalic acid and 2,5-di-α-naphthoylterephthalic acid are formed.[200]

The product obtained on condensing tetralin with pyromellitic anhydride and aluminum chloride is apparently a single isomeride of the possible ditetrahydronaphthoylbenzene dicarboxylic acids, assuming reaction at the β-position of tetralin. The product with decalin was not identified.[203]

Anhydrides of Heterocyclic Di- or Poly-carboxylic Acids

Nitrogen Ring Compounds

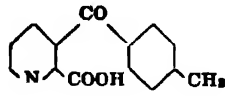
Quinolinic Acid Anhydride.—In 1887, Bernthsen and Mettegang [204] reported that quinolinic anhydride reacts like phthalic anhydride in the Friedel-Crafts reaction:



[197] E. Philippi and F. Auslaender, *Monatsh.*, 42, 1-4 (1921); *J. Chem. Soc. Abs.*, 120 (I), 738 (1921).
[198] G. Machek and H. Martin, *Monatsh.*, 56, 116-134 (1930); *Brit. Chem. Abs.-A*, 1157 (1930).
[199] E. Philippi, *Monatsh.*, 34, 705-717 (1913); *J. Chem. Soc. Abs.* 104 (I), 627 (1913).
[200] H. de Diesbach and V. Schmidt, *Helv. Chim. Acta*, 7, 644-658 (1924); *J. Chem. Soc. Abs.*, 126 (I), 1032 (1924).
[201] E. Philippi and R. Seka, *Monatsh.*, 43, 615-619 (1923); *J. Chem. Soc. Abs.*, 124 (I), 576 (1923).
[202] E. Philippi and R. Seka, *Monatsh.*, 43, 621-631 (1923); *J. Chem. Soc. Abs.*, 124 (I) 577 (1923).
[203] E. Philippi, R. Seka, and K. Funke, *Monatsh.*, 45, 261-266 (1925); *J. Chem. Soc. Abs.*, 128 (I), 556 (1925).
[204] A. Bernthsen and H. Mettegang, *Ber.*, 20, 1908-1910 (1887); *J. Chem. Soc. Abs.*, 52, 787 (1887).

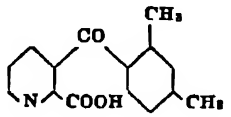
The formation of 3-benzoylpicolinic acid was later substantiated by Jeiteles, Kirpal, and Jephcott.[205] Kirpal [206] reported that the keto-acid was obtained in 92 per cent yield and that no isomer was formed in the reaction.

Condensation of quinolinic anhydride with toluene yields 3-(*p*-toluyl)-picolinic acid:



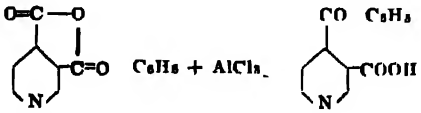
As with benzene, the analogous reaction with toluene leads only to the formation of derivatives of picolinic acid. Only the carboxyl group farthest removed from the nitrogen is effected, the anhydride residue attaching itself to the carbon residue in the *para*-position to the methyl group in toluene.[207]

m-Xylene yields the expected 3-(2,4-dimethylbenzoyl)picolinic acid [208]:



In the reaction with naphthalene two products, 3-[1 (and 2)-naphthoyl]picolinic acids were secured in a total yield of 22 per cent. Acenaphthene gives only a 10 per cent yield of 3-(4-acenaphthoyl)picolinic acid.[209] Biphenyl gives not only the expected 3-(*p*-phenylbenzoyl)picolinic acid, but also a good yield of 3-benzoylpicolinic acid. Although the condensations with naphthalene, acenaphthene, and biphenyl were all effected in benzene solution, the solvent reacted only in the experiment with biphenyl.[210]

Cinchomeronic Acid Anhydride.—Early investigators [211] report that the addition of cinchomeronic acid anhydride to benzene occurs with the formation of only 4-benzoylnicotinic acid:



[204] B. Jeiteles, *Monatsh.*, 17, 515 (1896) A Kirpal, *Monatsh*, 27, 371 (1906) C M Jephcott, *Trans Roy. Soc. Canada. (3)*, 18, Sect. III, 130 (1924); *C. Z.*, 1925 I, 1408

[205] A. Kirpal, *Monatsh.*, 31, 295-299 (1911); *C. A.*, 5, 1087

[206] A. Just, *Monatsh*, 18, 453-459 (1897); *J. Chem Soc Abs*, 74 (I), 42 (1898) H L Fulda *Monatsh.*, 21, 981 (1900). O. Halla, *Monatsh*, 32, 747-751 (1912), *C. A.*, 6, 360 C M Jephcott *loc. cit.*

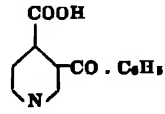
[207] O. Halla, *loc. cit*

[208] C. M. Jephcott, *Trans. Roy Soc Can. Sec. III (3)*, 19, 28 (1925); *C A*, 20, 764 (1926) C M Jephcott, *J. Am. Chem. Soc.*, 50, 1189-1199 (1928); *C. A.*, 22, 1975

[209] C. M. Jephcott. *J. Am. Chem Soc.*, 50, 1189-1192 (1928).

[210] A. Philips, *Ber*, 27, 1923-1927 (1894). M. Freund, *Monatsh.*, 18, 447-451 (1897). H L Fulda, *Monatsh.*, 20, 783-785 (1899).

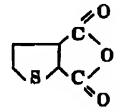
It has been shown by Kirpal,[212] however, that two isomeric keto-acids are really formed. Together with the acid noted above, he also obtained 3-benzoylisonicotinic acid,



Extraction of the reaction mixture with water dissolves out 4-benzoylnicotinic acid, leaving the isomeric acid undissolved. The presence of the slightest amount of 3-benzoylisonicotinic acid lowers the melting point of 4-benzoylnicotinic acid considerably; hence the lower values given to this acid by the early investigators. Kirpal reports the melting point of 4-benzoylnicotinic acid as 226° and that of 3-benzoylisonicotinic acid as 270°.

Sulfur Ring Compounds

Thiophene.—Friedel-Crafts reaction of thiophene-2,3-dicarboxylic acid anhydride,

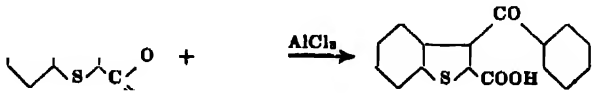


or its substitution products with phenols in which there are two adjacent unsubstituted carbon atoms has been claimed to result in the production of dyestuffs and intermediates.[213] The condensing agent may be aluminum chloride or a mixture of it with sodium chloride or ferric chloride. The products are hydroxy keto-acids.

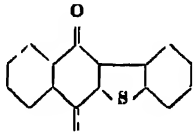
Thianaphthene.—The condensation of thianaphthene-2,3-dicarboxylic acid anhydride with aromatic hydrocarbons and phenols in the presence of aluminum chloride is of commercial importance in that it offers an efficient method for the preparation of dyestuffs of the thianaphthene series. Mayer and co-workers [214] report that whereas thianaphthene with phthalic anhydride in nitrobenzene solution gives a 33 per cent yield of 2-(2-thianaphthenoyl) benzoic acid,

[212] A. Kirpal, *Monatsh.*, 30, 355-361 (1909); *C. A.*, 4, 185 (1910).
[213] British P. 296,761 (1928) to I. G.; *C. Z.*, 1929 I, 448; U. S. P 1,765,687 (1930) to F. Mayer and K. Zahn (to General Aniline Works); *C. A.*, 24, 4056.
[214] F. Mayer (with A. Mombour, W. Lassmann, W. Werner, P. Landmann, and E. Schneider), *Ann.*, 458, 251-296 (1931).

the condensation of thianaphthene-2,3-dicarboxylic acid anhydride with benzene, using excess benzene as diluent, gives a 92 per cent yield of 3-benzoylthianaphthene-2-carboxylic acid:

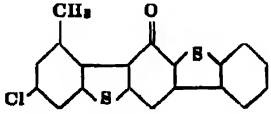


Since upon ring closure both keto-acids yield benzothiophanthrenequinone,



the advantage of using thianaphthene-2,3-dicarboxylic acid for the preparation of the quinone is obvious.

Condensation of the anhydride with naphthalene is effected by stirring for three days a mixture of the reactants with aluminum chloride in nitrobenzene solution. A 92 per cent yield of a mixture of keto-acids, convertible into benzobenzthiophanthrenequinones, is secured. In an analogous condensation of 6-chloro-4-methylthianaphthene with the thianaphthene-2,3-dicarboxylic acid anhydride, there is obtained 4-methyl-6-chloro-2,3'-dithianaphthenyl ketone 2'-carboxylic acid, but the yield is not so good as in the above-mentioned reactions. When the keto-acid is converted into its acid chloride and then treated with aluminum chloride in nitrobenzene, ring closure occurs, with formation of the bithianaphthenylquinone derivative:



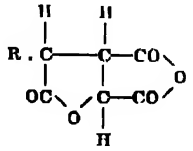
Mayer and his co-workers also describe the interaction of thianaphthene-2,3-dicarboxylic anhydride and hydroquinone in an $AlCl_3$-NaCl melt to give a 76 per cent yield of 7,10-dihydroxybenzothiophanthrenequinone.

Friedel-Crafts condensation of thianaphthene-2,3-dicarboxylic acid anhydride or its substitution products with aromatic hydrocarbons and phenols in the presence of aluminum chloride or an $AlCl_3$-NaCl melt is covered by several patents.[215]

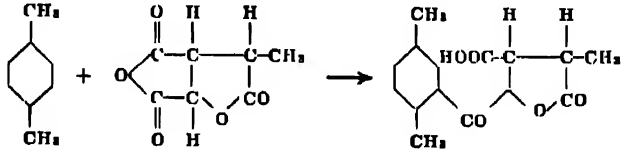
[215] British P. 261,383 (1926) to I. G., *Brit. Chem. Abs.*-B, 635 (1928); British P. 296,761 (1928) to I. G., *C. Z.*, 1929 I, 448; U. S. P. 1,765,957 (1930) to F. Mayer and K. Zahn (to General Aniline Works), *C. A.*, 24, 4056; German P. 512,237 (1930) to F. Mayer and K. Zahn (to I. G.), *C. Z.*, 1931 I, 1173; Swiss P. 137,740, 139,378 and 139,374 (1930) to I. G., *C. Z.*, 1930 II, 3863.

Oxygen Ring Compounds

It has been shown that anhydrides of *o*-dibasic lactonic acids of the type



condense with aromatic hydrocarbons or phenol ethers in the presence of aluminum chloride to give keto-lactonic acids.[216] Thus, reaction of 3-methylbutanolide dicarboxylic acid anhydride (m.p. 162°) and *p*-xylene proceeds according to the scheme:



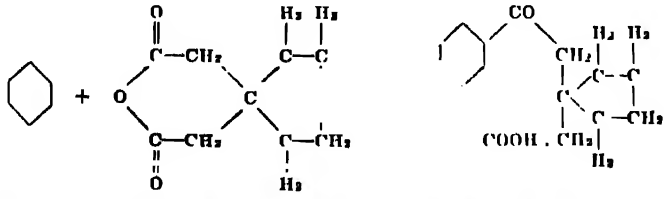
(I)

Condensation is effected by adding, with cooling, 17 g of aluminum chloride to a solution of 8.4 g of the anhydride and 12 g of *p*-xylene in 36 g of benzene, allowing the reaction mixture to stand for one day at 0° and then for two more days at ordinary temperature. The keto-acid I was obtained as the main product, 8 g of it being obtained as a white, crystalline product, m.p. 171-173°.

The anhydride was shown to undergo similar condensation with 6-methoxy-*p*-xylene.

Alicyclic Compounds

The anhydrides of cyclopentane-1,1-diacetic acid, 3-methylcyclopentane-1,1-diacetic acid, and cyclohexane-1,1-diacetic acid react with benzene or toluene and aluminum chloride in normal manner to give keto-acids.[217] With cyclopentane-1,1-diacetic acid anhydride reaction proceeds:

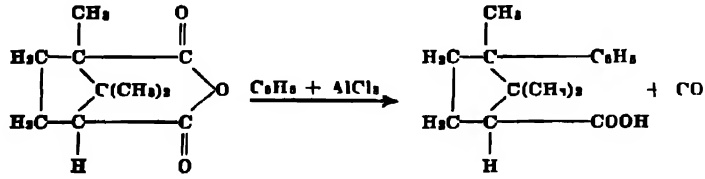


[216] A. E. Tschitschibabin and M. N. Schtschukina, *Ber.*, **63**, 2793-2806 (1930); *Brit. Chem. Abs.*-A, 89 (1931).

[217] A. Ali, R. D. Desai, R. F. Hunter, and S. M. M Muhammad, *J. Chem. Soc.*, 1013-1016 (1937). R. D. Desai and M. A. Wali, *Proc. Indian Acad. Sci.*, **6A**, 135-143 (1937); *C. A.*, **32**, 508 (1938). For the reaction of cyclopentane-1-carboxy-1-acetic anhydride with toluene and $AlCl_3$ to give α,α-cyclopentane-β-(*p*-toluyl)-propionic acid, see S. C. Sen-Gupta, *J. Indian Chem. Soc.*, **15**, 349-56 (1939). *C. A.*, **34**, 5242. For similar reaction with naphthalene and higher aromatic hydrocarbons, see S. C. Sen-Gupta, *J. Indian Chem. Soc.*, **17**, 101-106 (1940); *C. A.*, **34**, 5438.

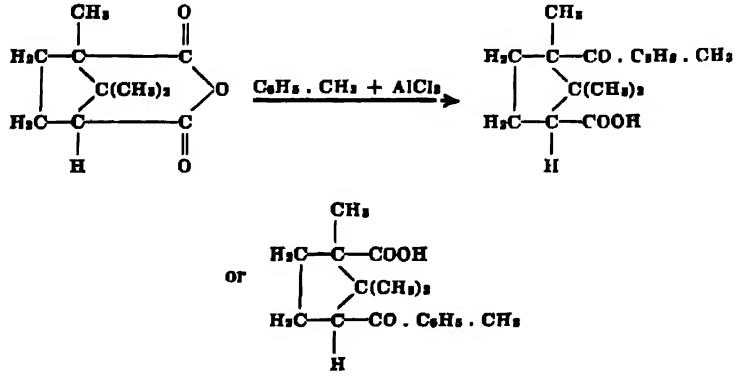
From 9 g of cyclopentane-1,1-diacetic anhydride there was obtained 8 g of the above product, 1-phenacylcyclopentane-1-acetic acid. Similar reaction with 3-methylcyclopentane- and cyclohexane-1,1-diacetic anhydrides yielded 1-phenacyl-3-methylcyclopentane-1-acetic acid and 1-phenacylcyclohexane-1-acetic acid, respectively. Only one product was obtained in each case.

Camphoric anhydride with benzene and aluminum chloride, according to Burcker,[218] yields phenylcamphoric acid (m.p. 142°) together with other products. Loss of carbon monoxide is involved.



The loss of carbon monoxide from camphoric anhydride when a chloroform solution of the anhydride is treated with an equal amount of aluminum chloride and allowed to stand over night has been noticed by several investigators.[219]

However, Eykman [220] observed no cleavage of carbon monoxide when he reacted toluene or anisole with camphoric anhydride in the presence of aluminum chloride. The condensation with toluene yielded a keto-acid (m.p. 187°) which was reported to be 1,1,2-trimethyl-2 (or 5)-toluylcyclopentanecarboxylic acid-5 (or 2):

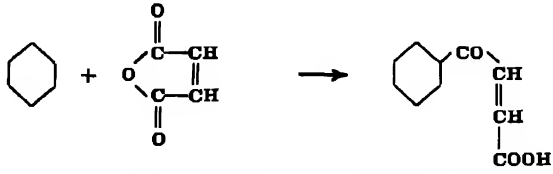


The condensation with anisole gives a product (m.p. 172°) the constitution of which is similar to that obtained with toluene, except that the anisyl residue is substituted for the tolyl residue.

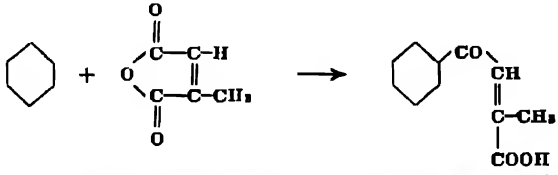
[218] E. Burcker, *Bull. soc. chim.* (3), 4, 113-118 (1890); *J. Chem. Soc. Abs.*, 60 (I), 324 (1891) E. Burcker and C. Stabil, *Compt. rend.*, 119, 426-428 (1894); *J. Chem. Soc. Abs.*, 68 (I), 108 (1895).
[219] F. H. Lees and W. H. Perkin, *J. Chem. Soc.*, 79, 356-361 (1901). W. H. Perkin and J. Yates, *J. Chem. Soc.*, 79, 1373-1386 (1901).
[220] J. F. Eykman, *Chem. Weekblad*, 4, 737-738 (1907); *C. Z.*, 1907 II, 2046.

Aliphatic Dicarboxylic Acid Anhydrides

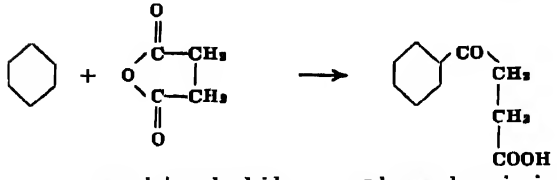
Friedel-Crafts condensations with anhydrides of aliphatic dicarboxylic acid anhydrides proceed as with phthalic anhydride. Reactions of the maleic, citraconic, succinic, pyrotartaric, and glutaric anhydrides with aromatic hydrocarbons or their derivatives or various heterocyclic compounds in the presence of aluminum chloride generally yield keto-acids, the condensations proceeding according to the schemes:



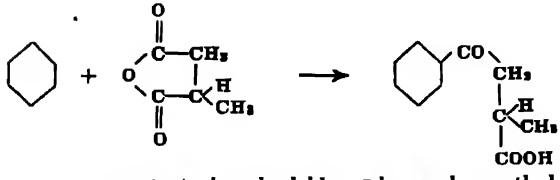
maleic anhydride — β-benzoylacrylic acid



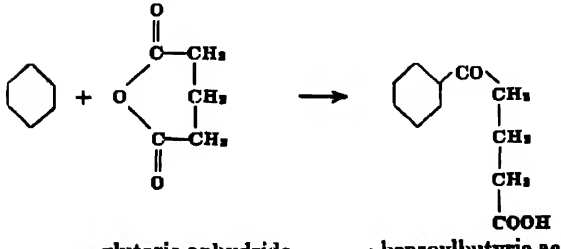
citraconic anhydride — α-methyl-β-benzoylacrylic acid



succinic anhydride — β-benzoylpropionic acid



pyrotartaric anhydride — β-benzoyl-α-methylpropionic acid



glutaric anhydride — γ-benzoylbutyric acid

Condensations have also been effected with the polyanhydrides of adipic and sebacic acids. Here not only is the ω-benzoyl fatty acid formed, but also a dibenzoyl alkane and a dibasic acid.[221]

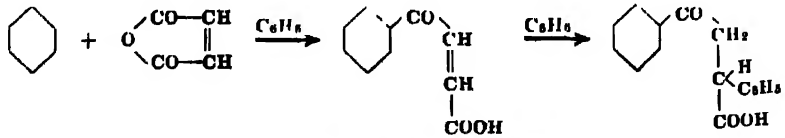
Although additions effected with aliphatic dibasic acid anhydrides are not as frequently complicated by the formation of isomeric product as are analogous reactions with phthalic anhydride, instances in which the condensation takes an anomalous course have been reported. These will be cited in the more detailed account of the individual reactions, which follows.

Maleic Anhydride

Condensations with Aromatic Hydrocarbons.—The production of β-benzoylacrylic acid was reported in 1882 by von Pechmann.[222] A few years later, Gabriel and Colman [223] gave a more thorough account of the condensation. These investigators gradually added 15 g of aluminum chloride to a solution of 10 g of the anhydride in 100 cc of benzene and heated the reaction mixture for six hours at 55-60°. A slow evolution of hydrogen chloride was noticed. The reaction product separated itself into two layers. The upper benzene layer contained the keto-acid. It crystallized out even upon cooling, but the addition of dilute sodium hydroxide gave a more complete precipitation. The crude keto-acid gave about 9 g of the pure acid upon recrystallization from boiling water.

In a study of a series of Friedel-Crafts reactions with maleic anhydride, Kozniewski and Marchlewski [224] recommend the preparation of β-benzoylacrylic acid by shaking 30 g of maleic anhydride in 1 liter of benzene with 40-50 g of aluminum chloride, heating after 24 hours for 10 to 15 hours at 40-50°, decomposition of catalyst complex with cold water and hydrochloric acid and separation of the benzene by steam distillation. The crude β-benzoylacrylic acid was found to contain some phenyl-γ-keto-α-hydroxybutyric acid, probably because of the presence of some malic anhydride in the maleic anhydride.

Recently, Pummerer and Buchta [225] showed that if the reaction were conducted in the presence of a large excess of the catalyst and of the hydrocarbon, disubstitution occurred. Thus, upon adding 75 g of finely powdered anhydrous aluminum chloride to a solution of 10 g of maleic anhydride in 10 cc of benzene and heating the reaction mixture for twelve hours, with stirring, there is obtained 4 g of α-phenyl-β-benzoyl-



[221] J. W. Hill, *J. Am. Chem. Soc.*, 54, 4105-4106 (1932); *C. A.*, 26, 5814.
[222] H. von Pechmann, *Ber.*, 15, 881-892 (1882); *J. Chem. Soc. Abs.*, 1074 (1883).
[223] S. Gabriel and J. Colman, *Ber.*, 32, 395-409 (1899).
[224] T. Kozniewski and L. Marchlewski, *Bull. Acad. Sci. Cracow*, 81-95 (1906); *J. Chem. Soc. Abs.* 90 (I), 750 (1906); *C. Z.*, 1906, II, 1139.
[225] R. Pummerer and E. Buchta, *Ber.*, 69, 1005-1017 (1936).

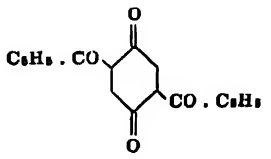
propionic acid, m.p. 148°. In this case there is addition of benzene to the olefinic bond.

That the formation of the disubstituted product occurs, with intermediate formation of β-benzoylacrylic acid, is evident from the fact that the same product is obtained upon treatment of the latter with benzene and aluminum chloride. With toluene under like conditions, the unsaturated keto-acid yields α-tolyl-β-benzoylpropionic acid.

Other investigators [226] report normal condensation of maleic anhydride with benzene, and point out that neither an excess of benzene nor of the anhydride interfere with the course of the reaction. The melting point of the pure β-benzoylacrylic acid is given as 97°; von Pechmann [222] had given 64° as the melting point of the hydrated acid.

The condensation of toluene with maleic anhydride has been reported by von Pechmann,[222] who secured β-toluylacrylic acid, m.p. 138°. Kozniewski and Marchlewski [224] also note the formation of the unsaturated keto-acid. Pummerer and Buchta obtained α-tolyl-β-toluylpropionic acid. They used the same procedure as that described above for the preparation of the phenyl homolog of this compound, except that 300 cc of toluene was used instead of 20 cc of benzene. β-Toluylacrylic acid was likewise shown to react with toluene and aluminum chloride to yield α-tolyl-β-toluylpropionic acid.

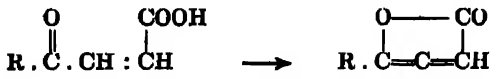
In describing the keto-acids obtained by him from maleic anhydride and benzene or toluene, von Pechmann [222] noted that upon heating them over their melting points, or by treatment with a dehydrating agent like acetic anhydride, acetyl chloride or phosphoryl chloride, they were converted into red, fluorescent substances. This transformation was subsequently investigated by Kozniewski and Marchlewski, who suggested that the substance obtained by heating β-benzoylacrylic acid with acetic acid was probably dibenzoylquinone,



and that the dyestuff obtained from β-toluylacrylic acid had an analogous structure. With the synthesis of 2,5-dibenzoylquinone, however, the foregoing structure has now been excluded as a possible structure for Pechmann dyes.[227]

The constitution of Pechmann dyes was subsequently investigated by Bogert and Ritter,[228] who suggested that, since the β-aroylacrylic acids under water cleavage were readily converted to highly unsaturated lactones,

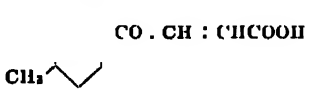
[226] G. P. Rice, *J. Am. Chem. Soc.*, 45, 222-238 (1923); M. T. Bogert and J. J. Ritter, *J. Am. Chem. Soc.*, 47, 826-835 (1925).
[227] R. Pummerer and E. Buchta, *Ber.*, 69, 1018-1021 (1936); *C. A.*, 30, 4854.
[228] M. T. Bogert and J. J. Ritter, *Proc. Nat. Acad. Sci. Washington*, 10, 363-367; *C. Z.*, 1924 II, 2333.



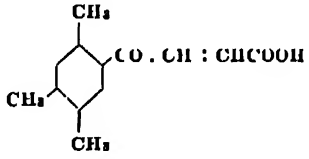
the Pechmann dyes were probably lactone addition products:

The lactone structure has been supported by Pummerer and Buchta,[229] who found that, upon dehydration, α-aryl-β-aroyl acids are readily converted to lactones of the diaryldihydrofuran series, which lose one atom of hydrogen under the influence of atmospheric oxygen with simultaneous doubling of the molecule.

The condensation of *m*-xylene, pseudocumene, or mesitylene with maleic anhydride and aluminum chloride has been reported by Kozniewski and Marchlewski [224] to yield β-*m*-xyloylacrylic acid (m.p. 114°),



β-pseudocumoylacrylic acid (m.p. 149°),



and β-mesitoylacrylic acid (m.p. 140.5°), respectively. In each case only one product was obtained. In an analogous condensation with *p*-*tert*-butyltoluene, however, Kozak [230] notes the formation of two keto-acids, one of which melts at 133-134° and the other at 115-117°. With *o*-*tert*-butyltoluene only one product, 4 (or 3)-methyl-3 (or 4)-*tert*-butylbenzoylacrylic acid (m.p. 123-124°), was secured.

In the reaction of naphthalene with maleic anhydride and aluminum chloride in dry benzene, a 70-80 per cent yield of a crude mixture of β-(1-naphthoyl)- and β-(2-naphthoyl)acrylic acids is secured. The crude product was shown to consist of 40 per cent of the 1-isomer and 60 per cent of the 2-isomer.[231]

Condensations with Phenol Ethers.—The reaction of phenol ethers with maleic anhydride in the presence of aluminum chloride has been reported to proceed either with formation of keto-acids or with the pro-

[229] R. Pummerer and E. Buchta, *Ber.*, **69**, 1005-1017 (1936).
[230] J. Kozak, *Bull. Acad. Sci. Cracow*, 407-417 (1906); *J. Chem. Soc. Abs.*, **92**, 403 (1907).
[231] M. T. Bogert and J. J. Ritter, *J. Am. Chem. Soc.*, **47**, 526-535 (1925).

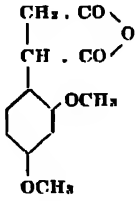
duction of succinic anhydride derivatives. Kozniewski and Marchlewski[224] obtained β-(4-ethoxybenzoyl)acrylic acid (m.p. 143-144°), by Friedel-Crafts condensation of maleic anhydride with phenetole. A 61 per cent yield of the acid (m.p. 143°) was secured by Eger[232] by gradual addition of 24 g of aluminum chloride to a solution of 18 g of phenetole and 10 g of maleic anhydride in 80 cc of carbon disulfide, placing the reaction flask in ice water until all the catalyst had been added, and then allowing the flask to stand for three hours in water kept at 40-50°. The keto-acid formed a pasty complex with aluminum chloride. This was transferred in small portions into a vessel of ice water; the volume of water was brought up to about 11 parts, and the residual carbon disulfide was removed by heating. The reaction mixture was filtered while hot; as the filtrate cooled, the keto-acid crystallized out.

The production of the acid in 62 per cent yield has been reported more recently by Rice[233] using carbon disulfide as solvent and an efficient electric stirrer, until the hardening of the addition product made stirring impossible. When the solid red cake was decomposed with ice and concentrated hydrochloric acid, the unsaturated keto-acid separated out as a solid and was filtered off with suction. Recrystallization from benzene gave yellow needles, m.p. 141-142°.

Recently, Dave and Nargund[234] reacted a number of phenol ethers with maleic anhydride in an attempt to secure derivatives of succinic anhydride. In every case, however, they secured benzoylacrylic acids. These investigators report the Friedel-Crafts preparation of the following:

β-(3-methyl-4-methoxybenzoyl)acrylic acid, m.p. 163°
β-(2-methoxy-5-methylbenzoyl)acrylic acid, m.p. 126°
β-(2-methyl-4-methoxybenzoyl)acrylic acid, m.p. 141°
β-(3,4-dimethoxybenzoyl)acrylic acid, m.p. 178°
β-(2,5-dimethoxybenzoyl)acrylic acid (methyl ester, m.p. 65°. b.p. 216°/42 mm.)

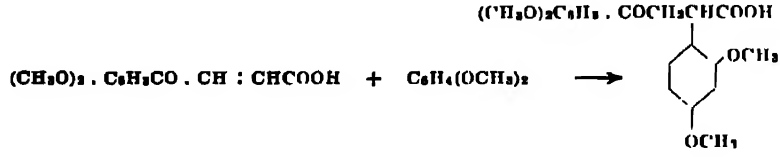
In 1931, however, Rice[235] had found that the condensation of resorcinol dimethyl ether with maleic anhydride and aluminum chloride proceeded mainly with the formation of (dimethoxyphenyl)succinic anhydride,



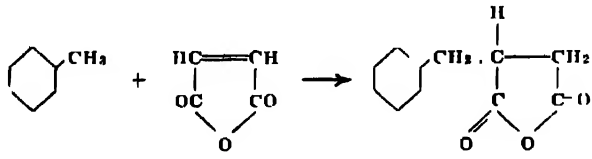
Reaction was effected by solution of 53 g of maleic anhydride in 71.5 g of the ether, gradual addition, under rapid stirring, of 150 g of carbon disulfide, and subsequent addition with ice cooling and constant stirring

[232] E. Eger, Dissertation, Heidelberg (1907).
[233] G. P. Rice, *J. Am. Chem. Soc.*, 46, 2319-2326 (1924).
[234] K. P. Dave and K. S. Nargund, *J. Univ. Bombay*, 1, Pt. 3, 191-195 (1933); *C. A.*, 33, 3779.
[235] G. P. Rice, *J. Am. Chem. Soc.*, 53, 3153-3159 (1931); *C. A.*, 25, 4895.

of 80 g of finely powdered aluminum chloride. There was isolated 49.2 g of the (dimethoxyphenyl)succinic anhydride noted above, 5.2 g of (dimethoxyphenyl)succinic acid, 5.6 g of (dimethoxybenzoyl)acrylic acid, and a small amount of α-(dimethoxyphenyl)-β-(dimethoxybenzoyl)propionic acid. Rice explains the formation of the succinic anhydride derivative by advancing a mechanism involving 1,4-addition to maleic anhydride and the formation of α-(dimethoxyphenyl)-β-(dimethoxybenzoyl)-propionic acid by addition of resorcinol at the double bond of the primarily formed (dimethoxybenzoyl)acrylic acid:

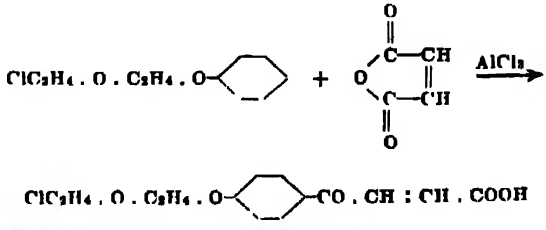


In connection with the work of Rice an I. G. Farbenindustrie patent [210] is of interest. It specifies the production of aryl derivatives of succinic anhydride by the reaction of maleic anhydride with aromatic hydrocarbons which have at least one saturated side chain, in the *absence* of Friedel-Crafts type catalysts. Addition takes place at the side-chain of the hydrocarbon without disruption of the maleic anhydride ring:



The anhydride of benzylsuccinic acid is formed according to the foregoing equation by heating 1000 parts of toluene with 98 parts of maleic anhydride in a pressure vessel for one-half hour at 305-315°. After this temperature has been held for 20 minutes a pressure of about 32 atmospheres is developed.

The reaction of β-phenoxyethoxyethyl chloride with maleic anhydride in carbon disulfide solution has been claimed to proceed normally, with formation of (β-chloroethoxyethoxy)benzoylacrylic acid [237]:

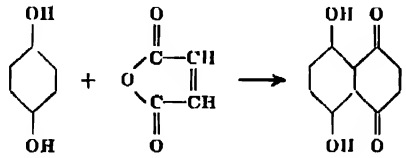


[236] German P. 607,380 (1935) to I. G.; *C. A.*, **29**, 1834.
[237] U. S. P. 2,122,675 (1938) to H. A. Bruson and J. W. Eastes (to Röhm and Haas); Brit. P. 506,-301 (1938) to Röhm and Haas.

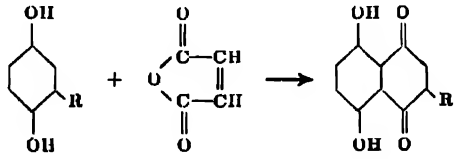
Condensation with Phenols in Solution.—β-(Hydroxybenzoyl)acrylic acid (m.p. 134.5°) has been obtained in 25 per cent yield from phenol, maleic anhydride, and aluminum chloride in benzene solution.[238]

Attempts to condense resorcinol with maleic anhydride and aluminum chloride in carbon disulfide have been reported to result only in conversion of the anhydride into fumaric acid.[228]

Use of $AlCl_3$-NaCl Melt with Phenols or Phenol Ethers.—Maleic anhydride and hydroquinone in an $AlCl_3$-NaCl melt at temperatures of over 200° yield naphthazarin [239]:



In the alkyl naphthazarins, the quinoid and benzenoid state of both rings appear to be exchangeable. Hence, the condensation of 3-alkyl hydroquinones under the same conditions results in the formation of naphthazarins in which the alkyl derivative is substituted in the quinone nuclei:



Kuroda and Wada [240] thus report the preparation of the following 3-alkyl naphthazarins:

	m.p. (°C)		m.p. (°C)
ethyl	126	*n*-butyl	86
propyl	118	isoamyl	96
isobutyl	89	isohexyl	100

Condensation with 2-alkyl hydroquinones proceeds analogously [241] with production of propyl-, *n*-butyl-, and isoamylnaphthazarins, m.p. 97°, 113°, and 91°, respectively.

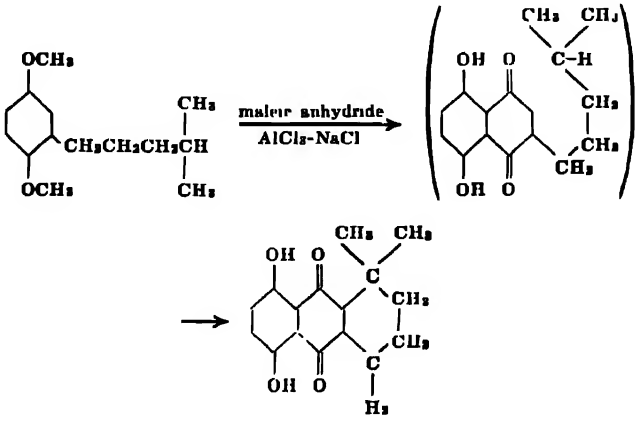
Brockmann and Müller [242] have prepared alkylated naphthazarins by reacting alkylated hydroquinone methyl ethers with maleic anhydride in an $AlCl_3$-NaCl melt. During the reaction, saponification of the methoxy groups occurs, with production, in rather good yields, of the following

[238] M. T. Bogert and J. J. Ritter, *J. Am. Chem. Soc.*, 47, 526-535 (1925).
[239] K. Zahn and P. Ochwat, *Ann.*, 462, 72-97 (1928); *C. A.*, 22, 3655. C. Kuroda and M. Wada, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 34, 1740-1761 (1938); *Brit. Chem. Abs.*-A, II, 168 (1939).
[240] C. Kuroda and M. Wada, *Proc. Imp. Acad. Tokyo*, 12, 239-241 (Nov., 1936); *C. Z.*, 1937 I, 3157.
[241] C. Kuroda and M. Wada, *Sci. Papers Inst. Phys. Chem. Res.*, 34, 1740-1761 (Nov. 1938), *C. Z.*, 1939 I, 2792.
[242] H. Brockmann and K. Müller, *Ann.*, 540, 51-72 (1939).

alkyl naphthazarins from the correspondingly alkylated hydroquinone ethers:

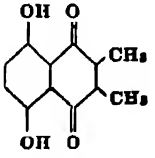
	m.p. (°C)		m.p. (°C)
ethyl	127	isobutyl	94
propyl	98	isoamyl	89

In the condensation of 3-isohexylhydroquinone dimethyl ether with maleic anhydride under the above conditions, isohexylnaphthazarin was not secured. Instead, the product was 1,1'-dimethyl-1,2,3,4-tetrahydroquinizarin (m.p. 83°), formed by ring closure of the intermediate alkyl naphthazarin:

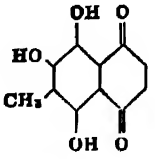


In the analogous reaction with 3-isohexylhydroquinone, however, Kuroda and Wada [243] reported only the formation of isohexylnaphthazarin.

Brockmann and Müller found that the condensation of 2,3-dimethylhydroquinone with maleic anhydride results in the formation of 2,3-dimethylnaphthazarin:



According to Kuroda and Wada,[241] however, 2-methyl-3-methoxyhydroquinone with maleic anhydride yields 7-hydroxy-6-methylnaphthazarin, m.p. 193°:



[243] C. Kuroda and M. Wada, *Proc. Imp. Acad. Tokyo*, 12, 239-241 (Nov., 1936); *C. Z.*, 1937 I, 3157

Substituted Maleic Anhydrides

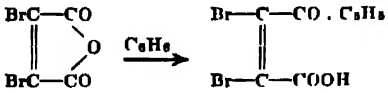
At the time that von Pechmann [222] reported the synthesis of β-benzoylacrylic acid from maleic anhydride, benzene, and aluminum chloride, he also stated that the analogous reaction with citraconic anhydride and benzene yielded β-benzoylcrotonic acid, $C_6H_5CO.C(CH_3):CHCOOH$, m.p. 113°. According to Bogert and Ritter,[231] however, the reaction results only in the production of α-methyl-β-benzoylacrylic acid (m.p. 153°), secured by these investigators in 20 per cent yield.

It has been reported by Kozniewski and Marchlewski [244] that citraconic anhydride and methylpropylmaleic anhydride undergo Friedel-Crafts reaction with aromatic hydrocarbons only with great difficulty, and that diphenylmaleic anhydride apparently does not react at all.

The condensation of methylethyl maleic anhydride with hydrocarbons and aluminum chloride, and the action of dehydrating agents on the resulting keto-acids has been studied by Marchlewski.[245]

In an $AlCl_3$-NaCl melt, citraconic anhydride and hydroxyhydroquinone yield 6(or 7)-hydroxy-2-methylnaphthazarin.[241] Under like conditions, toluhydroquinone gives 2,6(or 7)-dimethylnaphthazarin and 2,3-dimethylhydroquinone affords 2,3,6-trimethylnaphthazarin.[242]

Condensation of dibromomaleic anhydride with aromatic hydrocarbons is described by Lutz.[246] Upon warming gently for 30 minutes a mixture of 150 g of dibromomaleic anhydride, 120 g of aluminum chloride, and 300 cc of benzene, and then heating on a boiling water-bath for 15 minutes, a pasty mass is obtained from which 124 g (63 per cent yield) of crude *cis*-β-benzoyldibromoacrylic acid is secured:



Analogous reaction with mesitylene, effected by refluxing the reactants for 20 minutes, gives a 79 per cent yield of *cis*-β-(2,4,6-trimethylbenzoyl)-dibromoacrylic acid.

Succinic Anhydride

The preparation of β-benzoylpropionic acid from benzene and succinic anhydride in the presence of aluminum chloride was first reported by Burcker [247] and a few years later by Gabriel and Colman,[248] who gave a more detailed description of the reaction.

Kohler and Engelbrecht [249] secured 60-75 per cent yields of the acid (m.p. 116.5°) by first grinding together 70 g of dry succinic anhydride with 100 g of powdered aluminum chloride, gradually adding with stirring

[244] T. Kozniewski and L. Marchlewski, *Bull. Acad. Sci. Cracow*, 81-95 (1906); *C. Z.*, 1906 II, 1191.
[245] L. Marchlewski, *Z. physiol. Chem.*, 38, 196-197 (1903); *J. Chem. Soc. Abs.*, 1903 I, 667.
[246] R. E. Lutz, *J. Am. Chem. Soc.*, 52, 3405-3422 (1930).
[247] E. Burcker, *Ann. chim. phys. (5)* 26, 435 (1882); *Bull. soc. chim. (2)*, 35, 17 (1881); *J. Chem. Soc. Abs.*, 279 (1881).
[248] S. Gabriel and J. Colman, *Ber.*, 32, 395-409 (1899).

350 g of dry benzene, and then allowing the reaction mixture to stand for 10 to 12 hours at room temperature. Somerville and Allen [250] added in one portion with stirring, 200 g of aluminum chloride to a mixture of 68 g of succinic anhydride and 350 g of benzene, and heated the reaction mixture under reflux and continued stirring for one-half hour. They obtained 77-82 per cent yields of the impure acid, m.p. 111-113°. The pure acid melts at 116°.

Skraup and Schwamberger [251] secured 10 g of the acid by adding, in 4 portions with mechanical stirring during the course of six hours, 10 g of aluminum chloride to a mixture consisting of 10 g of succinic anhydride and 100 g of benzene.

The condensation of succinic anhydride and toluene, with formation of β-*p*-toluylpropionic acid, has been described by various investigators [252] Katzenellenbogen secured a 47 per cent yield by dissolving 20 g of the anhydride in 100 g of hot toluene, cooling the solution, adding gradually 30 g of aluminum chloride to it, and heating the reaction mixture for six to eight hours at 40-50°.

De Barry Barnett and Sanders [253] have reacted a series of alkylbenzenes with succinic anhydride. Condensation was effected by slowly adding 60 g of aluminum chloride to a mixture of 0.2 mole of the anhydride and 0.22 mole of the hydrocarbon in 75 cc of *sym*-tetrachloroethane Reaction was rapid at room temperature and was completed in two to three hours, except with *p*-xylene, in which case the reaction mixture was allowed to stand over night. The method gave 80-90 per cent yields of the following alkyl-substituted β-benzoylpropionic acids from the corresponding hydrocarbons:

	m.p. (°C)		m.p. (°C)
4-methyl	129	2,4-dimethyl	114
4-isopropyl	142	2,5-dimethyl	
3,4-dimethyl	129		

Friedel-Crafts reaction of mesitylene with succinic anhydride has been reported [254] to yield a β-mesitoylpropionic acid, m.p. 107°.

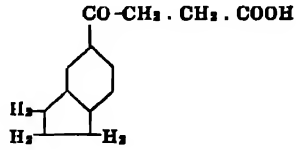
Addition of aluminum chloride to a mixture of succinic anhydride and ethylbenzene in benzene has been reported by Lévy [255] to result in production of β-(4-ethylbenzoyl)propionic acid, m.p. 102-103°.

tert-Butylbenzene, succinic anhydride, and aluminum chloride in carbon disulfide gives a 55 per cent yield of β-(4-*tert*-butylbenzoyl)propionic acid, m.p. 121-122°.[256]

[250] E. P. Kohler and H. Engelbrecht, *J. Am Chem Soc*, 41, 764-770 (1919).
[251] L. F. Somerville and C. F. H. Allen, *Org. Syntheses*, 13, 12-14 (1933)
[252] S. Skraup and E. Schwamberger, *Ann.*, 462, 135-158 (1928)
[253] E. Burcker, *Bull. soc. chim (2)*, 49, 449 (1888); *Ann chim phys. (5)*, 26, 437 (1882). F. Muhr *Ber.*, 22, 3215-3218 (1889). A. Katzenellenbogen, *Ber.*, 34, 3828-3839 (1901) H. Limpricht, *Ann.*, 312, 110-117 (1900). W. Borsche, *Ber.*, 47, 1106-1121 (1914)
[254] E. de Barry Barnett and F. G. Sanders, *J. Chem. Soc.*, 434-437 (1933).
[255] C. F. H. Allen, J. B. Normington, and C. V. Wilson, *Can. J. Research*, 11, 382-394 (1934).
[256] G. Lévy, *Ann. Chim. (11)*, 9, 5-87 (1938); *Brit. Chem Abs.-A*, II, 80 (1938).
[257] L. F. Fieser and C. C. Price, *J. Am. Chem. Soc*, 58, 1838-1843 (1936); *C. A.*, 30, 8221.

A 10 g yield of β-(4-chlorobenzoyl)propionic acid (m.p. 131°) has been obtained by heating at 40-50°, until evolution of hydrogen chloride has ceased, a mixture consisting of 120 g of chlorobenzene, 10 g of succinic anhydride, and 15 g of aluminum chloride.[257]

Hydrocarbons containing condensed nuclei also react with succinic anhydride; thus hydrindene produces γ-keto-γ-5-hydrindylbutyric acid,[258]



Naphthalene may produce a mixture of naphthoylpropionic acids. Borsche and Sauernheimer [259] conducted the reaction at 50-60° and obtained only β-2-naphthoylpropionic acid, but Giua [260] obtained both the 1- and 2-isomeric acids when reaction was carried on in the cold, and observed that heat increased the proportion of the 2-isomer. Haworth [261] obtained better results by conducting the reaction in a solvent, such as nitrobenzene or carbon disulfide, with a 50 per cent excess of hydrocarbon; Fieser and Peters,[262] obtained still better results with a 10 per cent excess of anhydride.

Haworth and his co-workers and Fieser and Peters conducted the condensation of alkyl naphthalenes with succinic anhydride in nitrobenzene solution. Some of these preparations are listed:

Alkyl naphthalene	-propionic acid	Ref.
1-Methyl	β-(4-methyl-1-naphthoyl)- (80% yield)	2
2-Methyl	β-(6-methyl-2-naphthoyl)- (19 g from 14 g of hydrocarbon and 10 g of the anhydride)	3
2-Methyl	β-(2-methyl-1-naphthoyl)-	4
β-Isopropyl	β-(6-isopropyl-2-naphthoyl)-	3
2,3-Dimethyl	β-(6,7-dimethyl-2-naphthoyl)- (70% yield)	1
2,7-Dimethyl	β-(2,7-dimethyl-1-naphthoyl)-	4

References

1 R. D. Haworth and F. M. Bolam, *J. Chem Soc.*, 2248-2254 (1932).
2. R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, 2720-2723 (1932).
3. R. D. Haworth, B. L. Letsky, and C. R. Mavin, *J. Chem. Soc.*, 1784-1792 (1932).
4. L. F. Fieser and M. A. Peters, *J. Am. Chem. Soc.*, 54, 4347-4356 (1932).

[257] S. Skraup and E. Schwamberger, *loc. cit.*; *cf.* C. F. H. Allen, J. B. Normington, and C. V. Wilson, *loc. cit.*
[258] S. C. Sen Gupta, *Current Science*, 5, 133 (1936); *C. A.*, 31, 5789 (1937). L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, 59, 883-887 (1937).
[259] W. Borsche and H. Sauernheimer, *Ber.*, 47, 1645-1648 (1914).
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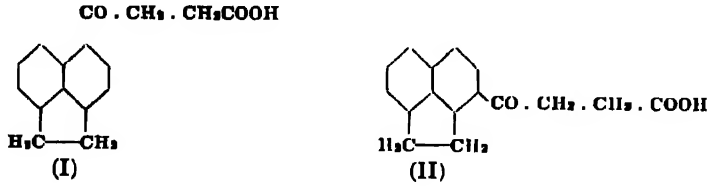
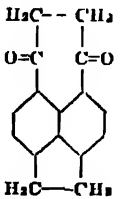
[261] R. D. Haworth, *J. Chem. Soc.*, 1125-1133 (1932).
[262] L. F. Fieser and M. A. Peters, *J. Am. Chem. Soc.*, 54, 4347-4356 (1932).

Fieser and Peters[263] studied the condensation of acenaphthene with succinic anhydride in the presence of aluminum chloride and nitrobenzene at 0° and −15°, and observed the formation of two isomeric products β-(3-acenaphthoyl)propionic acid (I) and β-(1-acenaphthoyl)propionic acid (II)



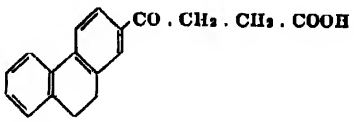
with (I) the predominant product. As an interesting reaction it was further observed that heating (I) with an $AlCl_3$-NaCl melt at 150° gave rise to the formation of *peri*-succinoylacenaphthene,



Condensation of biphenyl with succinic anhydride and aluminum chloride in nitrobenzene solution proceeds normally, with formation of β-(4-phenylbenzoyl)propionic acid in 70 per cent yield.[263a]

The condensation of anthracene and succinic anhydride produces β-(2-anthroyl)propionic acid in only about a 10 per cent yield.[264]

Tetralin, with succinic anhydride in the presence of aluminum chloride in nitrobenzene solution, gives a 90 per cent yield of β-6-(1,2,3,4-tetrahydronaphthoyl)propionic acid.[265] Phenanthrene derivatives condense in an analogous manner; for example, 9,10-dihydrophenanthrene produces β-2-(9,10-dihydrophenanthroyl)propionic acid,[266]



and retene forms a 6-retoylpropionic acid,[267]

[263] L. F. Fieser and M. A. Peters, *loc. cit.*; *cf.* French P. 636,065 (1928), Swiss P. 131,059 (1929) to I. G., U. S. P. 1,750,111 (1930) to H. Gruenu; German P. 376,635 (1923) to F. Mayer; L. F. Fieser, *Organic Syntheses*, 20, 1-5 (1940).

[263a] D. H. Hey and R. Wilkinson, *J. Chem. Soc.*, 1030 (1940).

[264] L. F. Fieser and M. A. Peters, *loc. cit.* J. W. Cook and A. M. Robinson, *J. Chem. Soc.*, 505-513 (1938). E. Bergmann and A. Weizmann, *J. Chem. Soc.*, 1242-1244 (1938); German P. 376,635 (1923) to F. Mayer.

[265] C. L. Hewett, *J. Chem. Soc.* 1940, 293-303.

[266] A. Burger and E. Mosettig, *J. Am. Chem. Soc.*, 59, 1302-1307 (1937).

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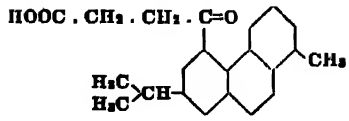

Chrysene suspended in benzene and reacted with succinic anhydride and aluminum chloride yields β-(2-chrysenoyl)propionic acid as well as some β-benzoylpropionic acid. A temperature of 35-40° seems to be the optimum for the production of the chrysene derivative.[268]

The reaction of 4,5-methylenephenanthrene with succinic anhydride and aluminum chloride in nitrobenzene solution results in the production of β-(4,5-methylene-1-phenanthroyl)propionic acid in 45.4 per cent yield. 9,10-Dihydro-4,5-methylenephenanthrene undergoes succinoylation only in one position, β-(4,5-methylene-9,10-dihydro-2-phenanthroyl)propionic acid being secured in 99 per cent yield.[269]

Condensation with Phenol Ethers.—Succinic anhydride condenses readily with phenol ethers. Reaction is generally effected by treating with aluminum chloride under cooling, and then allowing the reaction mixture to stand at room temperature. The yield may increase with the time of standing. For example, in the preparation of β-(2-methoxy-1-methyl-6-naphthoyl)propionic acid from 1-methyl-2-naphthyl methyl ether and succinic anhydride in nitrobenzene solution, the yield is 41 per cent after standing for 40 hours, 63 per cent after standing for three days, and 78 per cent after five days.

Solvents have been shown to have a decided influence on the course of the reactions. Consequently, they have been indicated in the list of preparations effected with phenol ethers and succinic anhydride which are shown in Table 29.

Condensations with Phenols.—The reaction of phenols with succinic anhydride has been shown to proceed normally if condensation is effected at 120-135° in *sym*-tetrachloroethane solution. Use of nitrobenzene and higher temperatures gives poor results. Products which have been obtained from phenols and the cresols are listed [270]:

Phenol	-propionic acid	m.p. (°C)
Phenol	β-(2-hydroxybenzoyl)- and β-(4-hydroxybenzoyl)-	
o-Cresol	β-(4-hydroxy-3-toluyl)- and β-(2-hydroxy-3-toluyl)-	184 136–7
m-Cresol	β-(2-hydroxy-4-toluyl)- and β-(4-hydroxy-2-toluyl)-	154 172
p-Cresol	only β-(2-hydroxy-5-toluyl)-	

[268] H. Beyer, *Ber.*, 71, 915-922 (1938); German P. 653,912 (1937) to I. G. (to H. Vollmann and H. Becker), *C. Z.*, 1938 I, 3065.

[269] L. F. Fieser and J. Cason, *J. Am. Chem. Soc.*, 62, 1293-1298 (1940). For the reaction of 4-methylphenanthrene with succinic anhydride and $AlCl_3$ to yield β-(5-methyl-3-phenanthroyl propionic acid, see W. E. Bachmann and R. O. Edgerton, *J. Am. Chem. Soc.*, 62, 2550-2553 (1940).

[270] J. D. Raval, K. V. Bokil, and K. S. Nargund, *J. Univ. Bombay*, 7, Pt. 3, 184-188 (1938); *C. A.*, 33, 5778.

Table 29 Condensations with Phenol Ethers

Ether	propionic acid	Solvent	% Yield	Ref
Anisole	β (p-methoxybenzoyl)-	CS_2		1 2
		$C_6H_5NO_2$		3
Phenetole	β (p-methoxybenzoyl)-	excess of phenetole	59%	4 7
Diphenyl ether	β-(p-phenoxybenzoyl)	CS_2	93	21
Veratrole	β (3 4 dimethoxybenzoyl)	CS_2	46	10
		CS_2		1 5
		$C_6H_5NO_2$	44	10
		$C_6H_5NO_2$	38 7	12
		$C_2H_2Cl_4$	64	10
Guaiacol	no reaction	CS_2		10
		$C_6H_5NO_2$		10
		$C_2H_2Cl_4$		10
Resorcinol dimethyl ether	β (2 4-dimethoxybenzoyl)	CS_2	50	10
		CS_2		1 6
		$C_6H_5NO_2$	88	10
		$C_2H_2Cl_4$	60	10
Resorcinol monomethyl ether	β (2-hydroxy 4-methoxybenzoyl)	CS_2	50	10
		$C_6H_5NO_2$	88	10
		$C_2H_2Cl_4$	60	10
Hydroquinone dimethyl ether	β (2 5 dimethoxybenzoyl)	CS_2	40	10
		CS_2		1
		$C_6H_5NO_2$	70	10
		$C_2H_2Cl_4$	45	10
Hydroquinone monomethyl ether	no reaction	CS_2		10
		$C_6H_5NO_2$		10
		$C_2H_2Cl_4$		10
Orcinol dimethyl ether	β (2 4 dimethoxy-6-methylbenzoyl)	CS_2 $C_6H_5NO_2$ or $C_2H_2Cl_4$		25
Hydroxyhydroquinone trimethyl ether	β (2 4,5-trimethoxybenzoyl)	CS_2		1
Pyrogallol trimethyl ether	β-(2-hydroxy-3 4 dimethoxybenzoyl)-	CS_2		1
		CS_2 $C_6H_5NO_2$ or $C_2H_2Cl_4$		25
o Cresol methyl ether	β-(4-methoxy-3 methylbenzoyl)	$C_6H_5NO_2$		3 12
p-Cresol methyl ether	β (2 methoxy 3 methylbenzoyl)-	$C_6H_5NO_2$		3 12
m-Cresol methyl ether	β-(4-methoxy-2-methylbenzoyl)-	$C_6H_5NO_2$		3 12
3-Methyl-6-isopropylanisole (?)	β (4-methoxy-2-methyl-5-isopropylbenzoyl)-	$C_6H_5NO_2$		3
p-Xylyl methyl ether	β (4-methoxy-2 5 dimethylbenzoyl)-	$C_6H_5NO_2$	70	8
5-Methyl-2-ethylanisole	β (3-methyl-6 ethylanisoyl)-	$C_6H_5NO_2$	96	9
4-Ethyl-2-methoxytoluene	β-(2-methyl-5 ethylanisoyl)-	$C_6H_5NO_2$	80	9
β-Phenoxyethoxyethyl chloride	(β-chloroethoxyethoxy)-benzoyl-	CS_2		13
α Naphthol methyl ether	β-(4 methoxy 1 naphthoyl)-	CS_2	30-40	14
		CS_2		15
		$C_6H_5NO_2$	90-92	16
		$C_2H_2Cl_4$	90 92	16
		ligroin	40	16
		$C_6H_5NO_2$		17
α-Naphthol ethyl ether	α β (ethoxy naphthoyl) , m p 198°	CS_2		17
β-Naphthol methyl ether	β-(2-methoxy-1-naphthoyl)- (I)	$C_6H_5NO_2$		15
	β (6 methoxy-2-naphthoyl)- ,			
	1 part of (I) and 9 parts of β-(2-methoxy 6-naphthoyl)-	$C_6H_5NO_2$	45 (total)	22
	only 1	CS_2		22
	only 1	$C_6H_5NO_2$	..	22

Table 29—*(Continued)*

Ether	-propionic acid	Solvent	% Yield	Ref.
1-Methyl-2-methoxy-naphthalene	β-(2-methoxy-1-methyl-6-naphthoyl)-	$C_6H_5NO_2$	78	24
1-Methoxy-7-isopropyl-naphthalene	β-(1-methoxy-7-isopropyl-4 naphthoyl)-	benzene, or better in $C_2H_2Cl_4$		19
1,5-Dimethoxy-naphthalene	β-(4,8-dimethoxy-1-naphthoyl)-	$C_6H_5NO_2$ CS_2	85 21	18 18
1,5-Dimethoxy-naphthalene	β-(4-hydroxy-8-methoxy-1-naphthoyl)- (heating at 40-74°)	$C_2H_2Cl_4$	100	18
p-Methoxy biphenyl	a mixture of β-(4-methoxy-4'-xenoyl)- and β-(4-methoxy-3-xenoyl)-	$C_6H_5NO_2$	24.5 60	20

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17. M. Gius, *Gazz. chim. ital.*, 47 I, 89-92 (1917); *J. Chem. Soc. Abs.*, 112, 394 (1917).
18. Peter Hill, W. F. Short, and H. Stromberg, *J. Chem. Soc.*, 937-941 (1937).
19. S. Keimatsu, T. Ishiguro, and K. Sumi, *J. Pharm. Soc. Japan* 56, 588-599 (1936); *C. Z.*, 1937 I, 2188.
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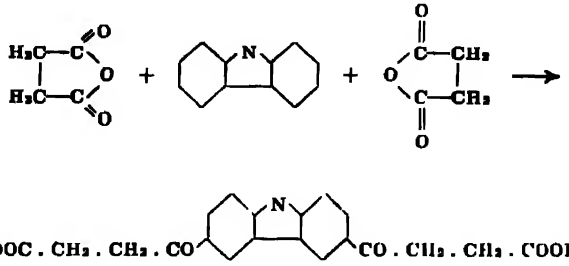
Monomethyl ethers of dihydroxy phenols do not undergo condensation with succinic anhydride as readily as do the dimethyl ethers. Dalal and Nargund [271] state that although veratrole and hydroquinone dimethyl ether easily react with succinic anhydride, no reaction occurs when guaiacol or hydroquinone monomethyl ether is treated with succinic anhydride and aluminum chloride under varying conditions. Resorcinol monomethyl ether does condense, but the yields of keto-acid are lower than they are in the analogous reaction with the dimethyl ether:

Solvent	% Yield of keto-acid from resorcinol monomethyl ether	% Yield of keto-acid from resorcinol dimethyl ether
Nitrobenzene	40	
Carbon disulfide	35	50
sym-Tetrachloroethane	40	60

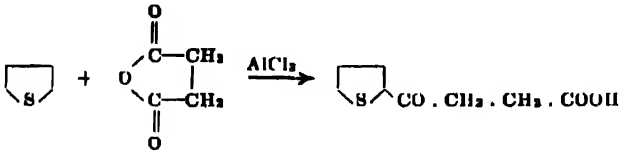
Condensation with Heterocyclic Compounds.—Two moles of succinic anhydride add to carbazole in Friedel-Crafts reactions. Upon slowly

[271] G. A. Dalal and K. S. Nargund, *J. Indian Chem. Soc.*, 14, 406-410 (1937); *C. Z.*, 1938 I, 4037.

adding 150 g of aluminum chloride to 30 g of carbazole and 45 g of succinic anhydride in 600 cc of freshly distilled nitrobenzene with good mixing and cooling, there is obtained 60-62 g of carbazole-3,6-bis-(keto-butyric acid)[272]:

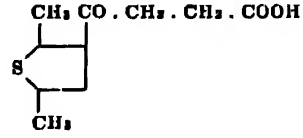


Thiophene reacts normally with succinic anhydride to give β-(α-thenoyl)propionic acid:

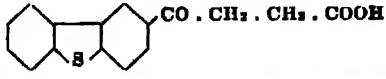


Addition during one hour of 288 g of aluminum chloride to a stirred mixture of 98 g of succinic anhydride, 80 g of thiophene, and 880 cc of nitrobenzene kept at 0-5°, and subsequent stirring of the reaction mixture for four hours results in a 54 per cent yield of the keto-acid. A 21 per cent yield is obtained when carbon disulfide is used as solvent.[273]

Analogously, addition of aluminum chloride during the course of three hours to a mixture of 2,5-dimethylthiophene and succinic anhydride in nitrobenzene at 0-5° and subsequent stirring for six hours yields 2,5-dimethylthenoyl-3-(β-propionic) acid[274]:



β-2-Dibenzothenoylpropionic acid,

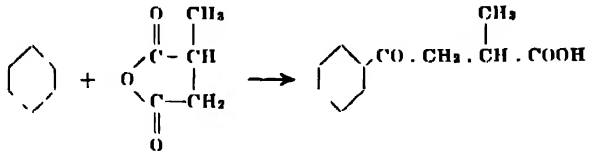


[272] R. Rajnowski and J. Susske, *Arch. Chem. Farm* 3, 135-140 (1937); *C. A.*, 32, 2639.
[273] L. F. Fieser and R. G. Kennelly, *J. Am. Chem. Soc.*, 57, 1611-1616 (1935); *C. A.*, 29, 7327
[274] W. Steinkopf, I. Poulsson, and O. Herdey, *Ann.*, 536, 128-134 (1938); *Brit. Chem. Abs.*-A (II) 503 (1938).

is obtained in 66 per cent yield when a suspension of 92 g of dibenzothiophene and 55 g of succinic anhydride in a mixture of 400 cc of *sym*-tetrachloroethane and 200 cc of nitrobenzene is treated with 150 g of aluminum chloride at 0-5°, and then hydrolyzed by ice and hydrochloric acid.[275]

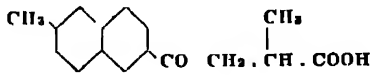
Substituted Succinic Anhydrides

Pyrotartaric anhydride adds to benzene in the presence of aluminum chloride to give β-benzoyl-α-methylpropionic acid[276]:

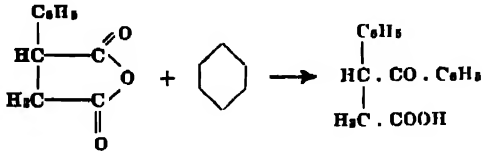


A 60 per cent theoretical yield of the acid is secured by adding, during ten minutes under cooling and shaking, 74 g of aluminum chloride to 37 g of the anhydride in 185 g of benzene, allowing the reaction mixture to stand for 30 minutes at room temperature, and then heating it at 40° for one hour, and finally at 100° for two hours.[277]

Condensation of pyrotartaric anhydride with 2-methylnaphthalene and aluminum chloride gives a 60 per cent yield of β-(6-methyl-2-naphthoyl)-α-methylpropionic acid,[278]



According to Anschütz and co-workers,[279] reaction of phenylsuccinic anhydride with benzene in the presence of aluminum chloride leads to addition of the benzene at the carbonyl group adjacent to the phenyl substituent, with production of β-benzoyl-β-phenylpropionic acid:



More recently,[280] however, the reaction has been reported to result in formation of the above acid (m.p. 168°) as well as in formation of the isomeric β-benzoyl-α-phenylpropionic acid (m.p. 154°)

[275] H. Gilman and A. L. Jacoby, *J. Org Chem.*, 3, 108-119 (1938); *C. A.*, 33, 579.
[276] T. Klobb, *Bull. soc. chim. (3)*, 23, 511-512 (1900); *J. Chem. Soc. Abs.*, 78 (I), 497 (1900).
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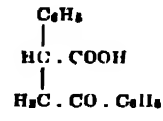
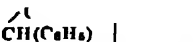
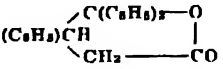


and a neutral product (m.p. 285°) probably the lactone of α-hydroxy-α,γ,γ-triphenyl-*n*-butyric acid,



or its β,γ,γ-triphenyl isomer,



When 30 cc of toluene and 10 g of phenylsuccinic anhydride are treated with 20 g of aluminum chloride there is produced 5 g of β-phenyl-β-*p*-toluylpropionic acid (m.p. 154°), and 3 g of α-phenyl-β-*p*-toluylpropionic acid, m.p. 150°. If the reaction is effected in nitrobenzene solution, and 5 g of the anhydride is used, there are obtained 3.5 g of α-phenyl acid and 0.6 g of the β-phenyl isomer.[281]

Condensation of phenylsuccinic anhydride with veratrole and aluminum chloride in nitrobenzene solution proceeds smoothly, giving an 84 per cent yield of β-veratroyl-α-phenylpropionic acid.[282] The condensation of *p*-methoxyphenylsuccinic anhydride with veratrole has been reported to be not so smooth a process as that of phenylsuccinic anhydride.[283]

However, it was later shown [284] that veratrole, hydroquinone dimethyl ether, and resorcinol dimethyl ether give the expected keto-acids when reacted with *p*-methoxyphenylsuccinic anhydride and aluminum chloride in appropriate solvent. With anisole or tolyl methyl ethers, *p*-methoxyphenylsuccinic anhydride gives normal reaction products also.[284a]

2,4-Dimethoxyphenylsuccinic anhydride reacts with resorcinol dimethyl ether and aluminum chloride in carbon disulfide solution to give a mixture of ketonic acids.[285]

α,α-Dimethylsuccinic anhydride undergoes Friedel-Crafts reaction with benzene to give the expected α,α-dimethyl-β-benzoylpropionic acid.[286] Diethylsuccinic anhydride reacts analogously.[286]

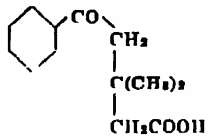
Condensation of isodibromosuccinic anhydride with benzene in the presence of aluminum chloride gives iso-β-benzoylacrylic acid dibromide (m.p. 142°) in an 80-85 per cent yield.[287]

[281] R. D. Desai and A. Wali, *Proc. Indian Acad. Sci.*, Sect. A5, 135-143, (Aug., 1937); *C. Z.*, 1937 II, 4311.
[282] R. Robinson and P. C. Young, *J. Chem. Soc.*, 1414-1418 (1935); *C. A.*, 30, 97.
[283] R. Robinson and J. Walker, *J. Chem. Soc.*, 1530-1533 (1935); *C. A.*, 30, 97.
[284] G. S. Savkar, K. V. Bokil, and K. S. Nargund, *J. Univ. Bombay*, 8, Part 3, 198-202 (1939); *Brit. Chem. Abs.-A*, 1940 II, 133.
[284a] G. A. Dalal, K. V. Bokil, and K. S. Nargund, *J. Univ. Bombay*, 8, Part 3, 190-197 (1939); *Brit. Chem. Abs.-A*, 1940 II, 133.
[285] G. P. Rice, *J. Am. Chem. Soc.*, 53, 3158-3159 (1931).
[286] S. C. Sengupta, *J. prakt. chem.*, 151, 82-96 (1938); *C. A.*, 32, 9041.
[287] M. T. Bogert and J. J. Ritter, *J. Am. Chem. Soc.*, 47, 526-535 (1925).

Anhydrides of Higher Aliphatic Dicarboxylic Acids

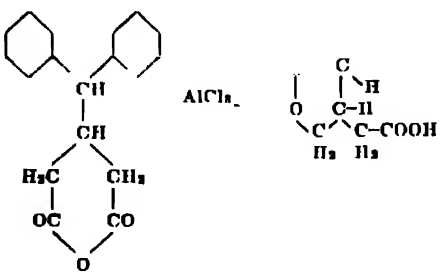
Addition of glutaric anhydride to benzene, effected by adding a benzene solution of glutaric anhydride to a suspension of aluminum chloride in benzene, and maintaining the reaction mixture at below 15° for 1½ hours results in production of γ-benzoylbutyric acid in 80-85 per cent yield.[288]

More recently [289] the reaction was effected by adding 16 g of aluminum chloride to a cooled solution of 7 g of the anhydride in benzene, and after twelve hours, heating the reaction mixture until hydrogen chloride was no longer evolved. There was secured 8.5 g of the γ-benzoyl-*n*-butyric acid, m.p. 132°. Smooth addition may also be effected with some substituted glutaric anhydrides.[289] From β,β-dimethylglutaric anhydride and benzene under analogous conditions, there is secured a good yield of γ-benzoyl-β,β-dimethyl-*n*-butyric acid, b.p. 115°/35 mm.



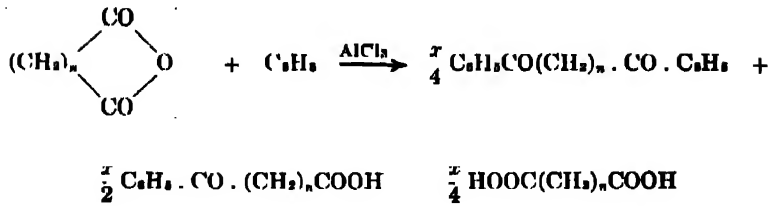
Similarly, β-methyl-β-ethylglutaric anhydride yields γ-benzoyl-β-methyl-β-ethyl-*n*-butyric acid, m.p. 49°. β-Phenylglutaric anhydride was found not to condense with benzene; instead, internal condensation to ketohydrindene-3-acetic acid occurred.

Intramolecular ring closure also occurs when β-benzohydrylglutaric anhydride is treated with aluminum chloride in *sym*-tetrachloroethane solution. 1,2,3,4-Tetrahydro-4-keto-1-phenyl-2-naphthaleneacetic acid is produced in 63 per cent yield [290]:



The polymeric anhydrides of adipic acid and sebacic acid react with benzene in presence of aluminum chloride to yield mixtures of the appropriate alkane, ω-benzoyl fatty acid, and dibasic acid:

[288] L. F. Somerville and C. F. H. Allen, *Org. Syntheses*, 13, 12-14 (1933).
[289] A. Ali, R. D. Desai, R. F. Hunter, and S. M. M. Muhammad, *J. Chem Soc.*, 1013-1016 (1937); *Brit. Chem. Abs.*-A, II, 840 (1937).
[290] M. S. Newman and L. M. Joshel, *J. Am. Chem. Soc.*, 62, 972-4 (1940).



Hill [291] found that the polyanhydride from adipic acid (prepared by refluxing with acetic anhydride for six hours) with benzene and aluminum chloride gives 75 per cent of ω-benzoylvaleric acid (m.p. 70-71°) and 85 per cent of dibenzoylbutane, m.p. 105-106°. In the same way sebacic polyanhydride gives 78 per cent of ω-benzoylnonanoic acid (m.p. 77-78°) and 86 per cent of dibenzoyloctane, m.p. 92-93°.

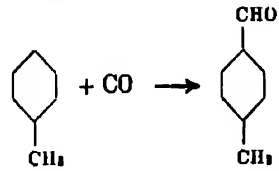
According to Plant and Tomlinson [292] crude adipic anhydride, prepared by refluxing the acid with an excess of acetic anhydride for six hours and then removing the volatile material under reduced pressure at 100°, is entirely unsatisfactory for preparing δ-anisoylvaleric acid and α,δ-dianisoylbutane. From 40 g of adipic anhydride, 60 cc of anisole, 60 g of aluminum chloride in 100 cc of carbon disulfide solution, upon refluxing for three hours, these investigators secured 14 g of the α-anisoylvaleric acid (m.p. 127°) and 15 g of α,δ-dianisoylbutane, m.p. 144°. The condensation with phenetole took a similar course, yielding α,δ-diphenetoylbutane (m.p. 127°) and δ-phenetoylvaleric acid, m.p. 110°.

[291] J. W. Hill, *J. Am. Chem. Soc.*, 54, 4105-4106 (1932); *C. A.*, 26, 5914.
[292] S. G. P. Plant and M. E. Tomlinson, *J. Chem. Soc.*, 1992-1994 (1935).

Chapter 10

Aldehyde Synthesis

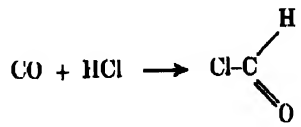
A very interesting application of aluminum chloride involves the synthesis of aromatic aldehydes. There are two generally applied methods. One of these, usually called the Gatterman-Koch reaction, employs carbon monoxide for the conversion of aromatic hydrocarbons to the corresponding aldehydes thus,



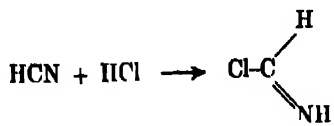
luminum chloride promotes this reaction in the presence of a small mount of water or hydrogen chloride and an activating agent such as uprous chloride. The use of pressure eliminates the necessity for an ctivator.

The foregoing reaction is unsuitable for the preparation of aldehydes f phenols or phenol ethers. However, by means of hydrogen cyanide in he presence of hydrogen chloride and aluminum chloride, these compounds are readily converted to the corresponding aldimides which in turn may be hydrolyzed to the aldehyde. This method of preparing aromatic aldehydes is known as the Gattermann synthesis. Zinc cyanide may be substituted for hydrogen cyanide with excellent results.

It is of interest to note that both of these reactions may be considered as Friedel and Crafts reactions, in the sense that both processes are believed to involve the primary formation of chlorides. In the Gattermann-Koch synthesis formyl chloride is first formed:



In the Gattermann reaction, imidoformyl chloride is an intermediate product:



These derivatives subsequently react with the aromatic compound according to the Friedel-Crafts reaction.

The synthesis of aromatic aldehydes by reaction of aromatic hydrocarbons with carbon monoxide in presence of hydrogen chloride and metal halide catalysts was first reported in 1897 by Gattermann and Koch,[1] and is generally known as the Gattermann-Koch aldehyde synthesis, to distinguish this method from the so-called Gattermann aldehyde synthesis which involves the use of cyanides.*

Gattermann and Koch prepared *p*-tolualdehyde from toluene by treating it with a mixture of hydrogen chloride and carbon monoxide in the presence of aluminum chloride and cuprous chloride. Only a trace of aldehyde was formed when aluminum chloride was used without cuprous chloride. Subsequent investigation [2] showed that the cuprous chloride may be replaced by nickelous, cobaltous, or ferric chloride, or by tungsten chloride. Nickelous chloride gives the best yields, but in no case are they much above 50 per cent of those obtained with cuprous chloride. The use of sulfuric acid, together with hydrogen chloride, was found advantageous.[3]

Gattermann was unable to prepare benzaldehyde with the aluminum chloride-cuprous chloride catalyst; he was able to react benzene with carbon monoxide and hydrogen chloride only if aluminum bromide were substituted for the aluminum chloride in the Gattermann-Koch aldehyde synthesis.[4] According to Reformatsky,[5] an 85-90 per cent theoretical yield of benzaldehyde is secured when a mixture of hydrogen chloride and carbon monoxide is passed through benzene containing freshly prepared aluminum bromide and cuprous chloride. The mechanism of the reaction was explained by assuming that hydrogen chloride and aluminum bromide give aluminum chloride and hydrogen bromide, and that the latter, in the nascent state and in the presence of cuprous chloride, then condenses with the carbon monoxide to form the bromoanhydride of formic acid, which subsequently reacts with benzene to yield hydrogen bromide and benzaldehyde.

It was later shown that the Gattermann-Koch aldehyde synthesis may be used for preparing benzaldehyde in presence of aluminum chloride if reaction is conducted in nitrobenzene solution at 50-60° and at atmospheric pressure.[6]

In 1914 it was announced that benzaldehyde is advantageously prepared if carbon monoxide is reacted with benzene in the presence of aluminum chloride under superatmospheric pressure.[7] The use of a little

[1] L. A. Gattermann and J. A. Koch, *Ber.*, 30, 1622-1624 (1897); *J. Chem. Soc. Abs.*, 72 (I), 510 (1897).

* See page 600.

[2] A. Korczynski and W. Mrozinski, *Bull. soc. chim. (4)*, 29, 459-462 (1921); *J. Chem. Soc. Abs.* 120 (I), 507 (1921).

[3] N. Schapiro, *Chem. Ztg.*, 50, 428 (1926); *C. A.*, 20, 2765.

[4] L. Gattermann, *Ann.*, 347, 347-386 (1906); *J. Chem. Soc. Abs.*, 90 (I), 589 (1906); *cf.*, German P. 98,709 (1898) to F. Bayer and Co., German P. 126,421 (1899) to Kuehler and Buff.

[5] A. Reformatsky, *J. Russ. Phys. Chem. Soc.*, 33, 154-157 (1901); *J. Chem. Soc. Abs.*, 80 (I), 327 (1901).

[6] German P. 403,489 (1921) to Gelsenkirchener Bergwerksgesellschaft.

[7] German P. 281,212 (1914) to C. F. Boehringer & Son; *C. Z.*, 1915 I, 178.

hydrogen chloride,[8] or of titanium chloride, either alone or in admixture with hydrochloric or sulfuric acid, was claimed to accelerate the pressure reaction of benzene with carbon monoxide in presence of aluminum chloride.[9] Holloway and Krase[10] have made a study of the reaction conditions for the synthesis of benzaldehyde from benzene and carbon monoxide under pressure. The reaction was studied at 25, 35, and 50° under carbon monoxide pressures of 1000 lb./sq. in. in apparatus especially designed[11] for establishing intimate contact between gases and liquids, or between gases, liquids, and solids under pressure. Factors affecting the yield of benzaldehyde were found to include water initially present, molar ratio of aluminum chloride to benzene, time, temperature, and carbon monoxide pressure. The presence of water was found to be necessary. At a given temperature, the rate of conversion was accelerated as the ratio of aluminum chloride to benzene was increased. At higher temperatures, however, the yield decreased as the ratio exceeded 0.5. Between 25 to 50° maximum conversion decreased with increasing temperature. Benzaldehyde was secured in 60-80 per cent yields, based on the benzene.

Several patents cover the pressure reaction of carbon monoxide and aromatic hydrocarbons in the presence of aluminum chloride. One reported continuous process consists of heating a benzenoid hydrocarbon or its halogenated derivative with carbon monoxide and aluminum chloride in the presence of small amounts of benzaldehyde and water at 20-50° and 350-2000 lb./sq. in. of pressure.[12] The reaction time may be decreased from 12 to 3½ hours if the condensation is effected in the presence of an aldehyde-aluminum chloride complex from a previous batch. At 25° and 68 atmospheres pressure, an 80 per cent yield of benzaldehyde, based on the aluminum chloride, is obtained.[13] Another technique omits the use of ice for hydrolysis. Improved conversion is secured by introducing carbon monoxide into an autoclave containing aluminum chloride and benzene which has been saturated at atmospheric pressure with water, and, upon completion of the reaction, discharging the reaction mass slowly into water maintained at 10-60°.[14]

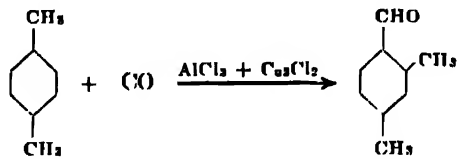
The production of aromatic aldehydes is claimed to be facilitated where first an addition compound of CO and HCl under pressure is prepared. This may be secured by leading a mixture of anhydrous hydrogen halide and carbon monoxide in molecular proportions at 20-250 atmospheres into a pressure vessel containing aluminum chloride.[15] The presence of copper, in at least equimolecular proportion to the aluminum chloride, is advantageous.[16]

[8] Brit. P. 3152 (1915); to J. Longman; *C. A.*, 10, 2126.
[9] Brit. P. 334,009 (1929) to I. G., *C. A.*, 25, 710; *Brit. Chem. Abs.*-B, 1016 (1930); U. S. P. 1,939,005 (1933) to General Aniline Works, *C. A.*, 28, 1356.
[10] J. H. Holloway and N. W. Krase, *Ind. Eng. Chem.*, 25, 497-502 (1933); *cf.* J. H. Holloway, *Chem. Age*, 27, 147 (1932); *C. Z.*, 1933, I, 415.
[11] A. H. Macmillan and N. W. Krase, *Ind. Eng. Chem.*, 24, 1001-1002 (1932); *C. A.*, 26, 5229.
[12] U. S. P. 1,935,914 (1933) to E. I. du Pont.
[13] U. S. P. 1,989,700 (1934) to A. T. Larson (to du Pont), *C. A.*, 29, 1834; Brit. P. 445,300 (1934) to A. T. Larson (to du Pont), *Brit. Chem. Abs.*-B, 695 (1936).
[14] Brit. P. 445,554 (1936) to E. I. du Pont; *C. A.*, 30, 6759
[15] Brit. P. 391,800 (1933) to I. G.; *Brit. Chem. Abs.*-B, 777 (1933)
[16] U. S. P. 1,976,583 (1934) to I. G.

A recently described [17] synthesis of toluene consists of primary pressure synthesis of benzaldehyde and subsequent reduction of the benzaldehyde to toluene. A 2:1 mixture of benzene and aluminum chloride is heated for four to eight hours at 30° in an autoclave containing carbon monoxide at 70-150 atmospheres pressure. About half the benzene is converted to benzaldehyde if secondary reactions are prevented by addition of a small amount of benzaldehyde or of a benzaldehyde-aluminum chloride complex. The benzaldehyde, diluted with an equal amount of benzene or toluene, is reduced to toluene by treatment with hydrogen under pressure at 300-360° in presence of molybdenum trisulfide on charcoal. Under favorable conditions 94 per cent of benzene can be converted into toluene.

p-Alkyl benzaldehydes may be prepared by reacting benzene simultaneously with carbon monoxide and with an agent adapted to introduce an alkyl group, in the presence of aluminum chloride.[18]

As has been pointed out by Gattermann,[4] alkyl benzenes undergo the Gattermann-Koch aldehyde synthesis more readily than benzene. Only one aldehyde group is introduced. The entering radical takes a position *p*- to an alkyl substituent present. If the *p*-position is not available, a displacement of the *p*-alkyl substituent may occur. Harding and Cohen [19] reported the formation of 2,5-dimethylbenzaldehyde from *p*-xylene; but it was later shown [20] that the reaction product, b. 219-229°, which was secured by these investigators is really 2,4-dimethylbenzaldehyde. Obviously, the *p*-alkyl group had migrated during the reaction:



Gattermann [21] found that aldehydes could not be prepared from phenolic ethers by means of carbon monoxide and hydrogen chloride in the presence of aluminum chloride and cuprous chloride because the latter was insoluble in the ethers in the presence of aluminum chloride.

Reactions effected with alkylated or halogenated benzenes and carbon monoxide in the presence of aluminum chloride under various conditions are listed:

[17] W. Demann, E. Krebs, and H. Borchers, *Tech. Mitt. Krupp Tech. Ber.*, 6, 59-63 (1938), *Brit. Chem. Abs.*-B, 1256 (1938), *C. A.*, 33, 6257.

[18] U. S. P. 2,158,513-9 (1939) to W. C. Neuly (to du Pont).

[19] E. P. Harding and L. Cohen, *J. Am. Chem. Soc.*, 23, 594-606 (1901); *J. Chem. Soc. Abs.*, 80 (I), 725 (1901).

[20] L. Francesconi and C. M. Mundici, *Gazz. chim. ital.*, 32, II, 467-494 (1902); *J. Chem. Soc. Abs.*, 84 (I), 426 (1903). C. M. Mundici, *Gazz. chim. ital.*, 34 (II), 114-122 (1904); *J. Chem. Soc. Abs.*, 86 (I), 897 (1904).

[21] L. Gattermann, *Ber.*, 31, 1149-1152 (1898).

Table 30

Aromatic Component	Added Component	Reaction Conditions	Aldehyde Secured	Ref.
Toluene	HCl + Cu_2Cl_2	5 hours	*p*-tolu-	1, 2
Toluene	HCl + Cu_2Cl_2	20°	*p*-tolu-	3
Toluene	titanium chloride + HCl	35–40°/60 atm. pressure	*p*-tolu-	7
Toluene	HCl	nitrobenzene solution	*p*-tolu-	8
Toluene		pressure	*p*-tolu-	10
o-Xylene	HCl + Cu_2Cl_2	35° for 7–8 hours	3,4-dimethyl-	1, 2
m-Xylene	HCl + Cu_2Cl_2		2,4-dimethyl-	1, 2
p-Xylene	HCl + Cu_2Cl_2		no reaction	1
p-Xylene	HCl + Cu_2Cl_2		2,5-dimethyl-	4
p-Xylene	HCl + Cu_2Cl_2		2,4-dimethyl-	5, 6
Mesitylene	HCl + Cu_2Cl_2	50° for 8 hours	only small amt. of 2,4,6-trimethylbenz-	1
Ethylbenzene	HCl + Cu_2Cl_2	20–25° for 3 hours	*p*-ethylbenz-	2
Cumene	HCl + Cu_2Cl_2	4 hours/30°	cuminol	1
Biphenyl	HCl + Cu_2Cl_2	6–8 hours/40°	biphenyl-4-	1
Biphenyl	HCl + Cu_2Cl_2	8 hours/35–40° and stand over night	biphenyl-4-	9
Hydrindene	HCl + Cu_2Cl_2	room temperature	hydrindene-5-	1
Chlorobenzene	titanium chloride + HCl	60°/50 atm. pressure	*p*-chlorobenz-	7
Chlorobenzene		pressure	*p*-chlorobenz-	10
Diisopropylbenzene	Cu_2Cl_2; with or without HCl	with or without pressure	diisopropylbenz-	11
Isopropylbenzene	as above	as above	diisopropylbenz- (and benzene as by-product)	11

References

1. L. Gattermann, *Ann.*, 347, 347-386 (1906); *J. Chem. Soc. Abs.*, 90 (I), 589 (1906).
2. L. Gattermann and J. A. Koch, *Ber.*, 30, 1622-1624 (1897); *J. Chem. Soc. Abs.*, 72 (I), 519 (1897).
3. G. H. Coleman and D. Craig, *Org. Syntheses*, 12, 80-83 (1932).
4. E. P. Harding and L. Cohen, *J. Am. Chem. Soc.*, 23, 594-606 (1901); *J. Chem. Soc. Abs.*, 80 (I), 725 (1901).
5. L. Francesconi and C. M. Mundici, *Gazz. chim. ital.*, 32 (2), 467-494 (1902); *J. Chem. Soc. Abs.*, 84 (I), 436 (1903).
6. C. M. Mundici, *Gaz. chim. ital.*, 34 (2), 114-124 (1904); *J. Chem. Soc. Abs.*, 86 (I), 897 (1904).
7. U. S. P. 1,939,005 (1933) to General Aniline Works, *C. A.*, 28, 1356; Brit. P. 334,009 to I. G., *C. A.*, 25, 710, *Brit. Chem. Abs.*-B, 1015 (1930).
8. German P. 403,489 (1921) to Gelsenkirchener Bergswerkgesellschaft.
9. D. H. Hey, *J. Chem. Soc.*, 2476-2479 (1931).
10. German P. 281,213 (1914) to C. F. Boehringer and Son, *C. Z.*, 1915 I, 178.
11. Brit. P. 288,708 (1929) to I. G. Farbenindustrie.

Nickel carbonyl condenses with benzene in the presence of aluminum chloride in the cold to give benzaldehyde. The yield obtained is not large, not exceeding 25 per cent of the weight of the benzene used. If the reaction is effected at 100°, only a trace of benzaldehyde is secured, the main product being an anthracene derivative. Toluene, *m*-xylene, and mesitylene similarly give small amounts of corresponding aldehydes in the cold, and anthracene derivatives upon heating. The formation of aldehydes is probably due to decomposition of the carbonyl, the resulting carbon monoxide reacting as in the Gattermann-Koch aldehyde synthesis. The formation of anthracene derivatives was assumed to be due to autocondensation of the aldehydes,[22] but Hey[23] has noted the formation of

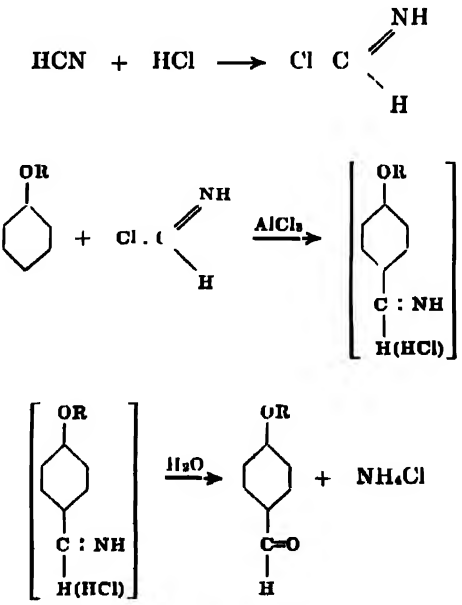
small amounts of anthracene in the Gattermann-Koch synthesis with benzene, and has assumed its presence to be due not to the condensation of two molecules of benzaldehyde, but to a series of reactions probably involving the decomposition of the aldehyde

$$C_6H_5.CHO \qquad C_6H_6 + CO$$

and a subsequent reaction of the carbon monoxide with aromatic hydrocarbons to provide the *meso-* carbon atoms in the anthracene molecule

Gattermann Aldehyde Synthesis

The Gattermann-Koch aldehyde synthesis, described in the preceding section, is unsuitable for the preparation of aldehydes of phenols or phenol ethers. Gattermann and his co-workers [24] found, however, that such aldehydes can be readily obtained in almost theoretical amount by the action of hydrogen cyanide and hydrogen chloride on the ether or phenol in presence of aluminum chloride. It was then postulated that the reaction proceeds with primary formation of imidoformyl chloride, and subsequent reaction with the phenol or phenol ether to give a primary aldimide. The latter is easily converted to the aldehyde upon heating with dilute acids [25]:



[24] J. Dewar and H. O. Jones, *J. Chem. Soc.*, **85**, 211-222 (1904); *cf.* A. Homer, *J. Chem. Soc.*, **91**, 1108-1141 (1907), *C. A.*, **2**, 76.

[25] D. H. Hey, *J. Chem. Soc.*, 72-75 (1935).

[24] L. Gattermann and C. Frenzel, *Ber.*, **31**, 1149-1152 (1898). L. Gattermann and W. Berchelmann, *Ber.*, **31**, 1765-1769 (1898). L. Gattermann and M. Köbner, *Ber.*, **32**, 278-283 (1899). L. Gattermann and F. Eggers, *Ber.*, **32**, 289-291 (1899). L. Gattermann, *Ann.*, **357**, 313-332 (1907).

[25] L. Gattermann, *Ann.*, **347**, 347-358 (1906).

The reaction has been applied to aromatic hydrocarbons, to furans, and to carboxy- and keto-derivatives of *m*-dihydroxybenzenes.

Studies of the Gattermann reaction applied to aromatic hydrocarbons has given an insight into the mechanism of the process. Hinkel and his co-workers [26] found that the $AlCl_3.2HCN$ complex seems to be too stable to give reaction below 40°. However, above this temperature, aromatic hydrocarbons are readily converted to the corresponding aldehydes. From a study of the action of bromine on hydrogen cyanide and its double compound with aluminum chloride ($AlCl_3 . 2HCN$) it has been shown that the latter compound is best represented as a molecular compound of aluminum chloride with imino-formalcarbylamine (bimolecular hydrogen cyanide), $AlCl_3.NH:CH\ NC$. With hydrogen chloride, it forms the complex $AlCl_3.NH:CH\ N:CHCl$, which upon heating dissociates into aluminum chloride and chloromethyleneformamidine, $NH:CH.N:CHCl$. These results support the hypothesis that chloromethyleneformamidine and not iminoformyl chloride is the active agent, according to the following scheme:

$$\begin{array}{l} NH:CH \\ \quad | \\ N:CHCl \end{array} \xrightarrow{C_6H_6} \begin{array}{l} NH:CH \\ \quad | \\ N:CHC_6H_5 \end{array} \xrightarrow{H_2O} NH_3 + HCO_2H + NH:CHC_6H_5$$

$$\xrightarrow{H_2O} NH_3 + C_6H_5.CHO$$

This mechanism, however, is not generally accepted and the majority of workers prefer to accept iminoformyl chloride as the reactive agent.

An attempt has been made to determine whether the reaction with phenols proceeds through intermediate condensation with the hydroxy-group, and subsequent rearrangement to aldimide.[27] In the absence of catalysts like aluminum chloride or zinc chloride, phenols were found to react readily with hydrogen cyanide in the presence of hydrogen chloride to yield imidoacyl aryl ester hydrochlorides

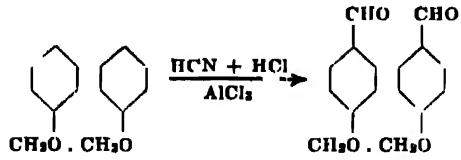
$$R.OH + HCN + HCl \longrightarrow R.O.CH:NH.HCl$$

but rearrangement into aldimine could not be effected. Obviously imido ester formation and nucleus condensation are independent reactions, the presence of aluminum chloride serving to suppress formation of ester and to favor introduction of the imino- group into the nucleus.

Introduction of the aldehyde group into the nucleus occurs at the *p*-position, if it is available. When the *p*-position is already occupied by a substituting group, *o*-hydroxy- or alkoxy- aldehydes are formed in small yields in the benzene series, and readily in the polynuclear series. Monosubstitution of the aldehyde group is the rule, but disubstitution has been secured with aryl ethers of glycols:

[26] L. E. Hinkel, E. E. Ayling, and W. H. Morgan, *J. Chem. Soc.*, 2793-2798 (1932). L. E. Hinkel, E. E. Ayling, and J. H. Beynon, *J. Chem. Soc.*, 339-346 (1936). L. E. Hinkel, Brit. P. 397,124 (1933); French P. 750,843 (1933) to Imperial Chemical Industries, Ltd., L. E. Hinkel and T. I. Watkins, *J. Chem. Soc.*, 1940, 407-409.

[27] J. Houben, *Ber.*, 59, 2878-2891 (1926); *C. A.*, 21, 1356 (1927).



Although biphenyl gives only a monoaldehyde, *o,o'*-dialkoxy- biphenyls yield dialdehydes. Resorcinol, orcinol, and phloroglucinol undergo the Gattermann aldehyde synthesis in absence of catalyst, in ether solution Resorcinol ethers require the use of a catalyst, but a mild catalyst like zinc chloride may be used.

The Gattermann aldehyde synthesis is effected by dissolving the phenol or phenol ether in benzene or ether, treating this with hydrogen cyanide and then adding aluminum chloride at room temperature, or preferably with cooling. Hydrogen chloride is then passed into the reaction mixture, first with cooling, then at room temperature, and finally under gentle warming, until the gas is no longer absorbed, usually for from one to four hours. Hydrolysis is effected by pouring the reaction mixture on ice, slightly acidified with hydrochloric acid. Unreacted phenol and the solvent are removed by fractional distillation. The method used for isolating the aldehyde depends upon its volatility. If it is volatile, it is separated during distillation; if not, by ether extraction or by conversion into the bisulfite. If the phenol used is not readily volatilized, the aldehyde may first be removed by treatment with sodium bisulfite, and the phenol removed by ether extraction. Various modifications of the procedure, directed especially at avoiding the preparation and handling of hydrogen cyanide, have been made. Johnson and Lane [28] have devised a method in which the hydrogen cyanide is passed into the reaction vessel directly from a generator. The use of zinc cyanide, instead of hydrogen cyanide, has given satisfactory results.[29] This method will be discussed later.

In Table 31 are listed some reported preparations of hydroxy- and alkoxy-aromatic aldehydes by Gattermann's method.

The use of zinc cyanide instead of hydrogen cyanide for the Gattermann aldehyde synthesis was first reported by Adams and Levine,[30] who found that resorcinol, orcinol, α- and β-naphthol, or pyrogallol condensed with hydrogen chloride and zinc cyanide in the absence of catalyst to give compounds that hydrolyzed readily to form hydroxy- aldehydes. Subsequently, Adams and Montgomery [31] investigated the use of aluminum chloride with the less reactive phenols. Phenols or phenol ethers and zinc cyanide were mixed with benzene as diluent, and hydrogen chloride was passed into the mixture, with cooling, until the saturation point had been reached. Aluminum chloride was then added and hydrogen

[28] T. B. Johnson and F. W. Lane, *J. Am. Chem. Soc.*, 43, 348-353 (1921).
[29] R. Adams and E. Montgomery, *J. Am. Chem. Soc.*, 46, 1518-1521 (1924).
[30] R. Adams and I. Levine, *J. Am. Chem. Soc.*, 45, 2373-2377 (1923).
[31] R. Adams and E. Montgomery, *J. Am. Chem. Soc.*, 46, 1518-1521 (1924).

Table 31

For solvents, B=benzene; E=diethyl ether.
For catalysts, Z=$ZnCl_2$; otherwise $AlCl_3$ has been used.
Reaction temperature given indicates maximum temperature used.
% yields are indicated in parentheses after product.

Phenol or Phenol Ether	HCN	Catalyst (g)	Temp. (°C)	Time (hrs)	Solvent	Product	Ref.
20 g Phenol	20 g	30	40	4	30 g B	*p*-hydroxybenzaldehyde (30%)	2, 11
10 g *o*-Cresol	10 g	15	40	..	10 g B	4-hydroxy-3-methylbenzaldehyde (40%)	2
10 g *m*-Cresol	10 g	15	..	..	15 g B	4-hydroxy-2-methylbenzaldehyde (50%)	2
p-Cresol	..	..	..	..	B	2-hydroxy-5-methylbenzaldehyde (5%)	1
4 g *o*-Ethylphenol	5 cc	8	..	3	30 g B	4-hydroxy-3-ethylbenzaldehyde (65%)	1
3,5-Diethylphenol	..	..	..	..	..	4-hydroxy-2,6-diethylbenzaldehyde	9
5 g *p*-Xylenol	5 g	10	40	3	20 g B	2,5-dimethyl-4-hydroxybenzaldehyde (80%)	1
p-Xylenol	..	..	..	..	B	above compd. and a little 2,5-dimethyl-6-hydroxybenzaldehyde	10
10 g *asym-o*-Xylenol	20 cc	20	30	6	60 g B	3,4-dimethyl-6-hydroxybenzaldehyde (low)	1
5 g 1,2,3-Xylenol	10 cc	15	40	7	50 g B	4-hydroxy-2,3-dimethylbenzaldehyde (60%)	1
20 g *sym-m*-Xylenol	20 cc	30	35	..	70 g B	4-hydroxy-2,6-dimethylbenzaldehyde	1
8 g *vic. m*-Xylenol	10 cc	15	40	..	80 g B	4-hydroxy-3,5-dimethylbenzaldehyde	1
6 g Carvacrol	6 cc	5	35	3	12 g B	4-hydroxy-5-methyl-2-isopropylbenzaldehyde (80%)	1
10 g Thymol	10 g	15	40	4	15 g B	4-hydroxy-2-methyl-5-isopropylbenzaldehyde	2
15 g α-Naphthol	15 cc	15 g Z	..	2.5	30 g B	4-hydroxy-1-naphthaldehyde (100%)	3
10 g α-Naphthol	10 g	10	35	2.5	50 g B	4-hydroxy-1-naphthaldehyde	2
15 g β-Naphthol	10 cc	15 g Z	..	2.5	30 g E	1-hydroxy-2-naphthaldehyde (100%)	3
5 g 1,5-Dihydroxynaphthalene	10 cc	5 g Z	0 20-25	..	40 cc E	1,5-dihydroxy-4-naphthaldehyde	1
5 g 2,7-Dihydroxynaphthalene	8 cc	6 g Z	0	1	40 cc E	2,7-dihydroxy-1-naphthaldehyde (100%)	1
5 g 2,6-Dihydroxynaphthalene	10 cc	5 g Z	0	1	45 cc E	2,6-dihydroxy-1-naphthaldehyde	1
10 g 3-Phenanthrol	14 cc	12	45	3	50 cc B	3-phenanthrol-4-aldehyde (70%)	13
Ten different dihydroxynaphthalenes	..	Z	..	..	E	hydroxynaphthaldehydes	19
10 g Resorcinol	5 cc	0	..	..	30 g E	2,4-dihydroxybenzaldehyde (100%)	2, 4, 8
1 part Resorcinol	50% excess	0	−5	..	3 parts E	2,4-dihydroxybenzaldehyde	15
Orcinol	..	0	..	..	E	4,6-dihydroxy-2-methylbenzaldehyde (100%)	4
7 g Cresorcinol	10 cc	15	..	3	60 g B	3-methyl-4,6-dihydroxybenzaldehyde (90%)	1
15 g Pyrogallol	15 g	40	40	2-3	80 g B	2,3,4-trihydroxybenzaldehyde (50%)	2

Table 31—*(Continued)*

Phenol or Phenol Ether	HCN	Catalyst (g)	Temp. (°C)	Time (hrs)	Solvent	Product	Ref
2 g Phloroglucmol	2 g	0	..	..	15 g E	2,4,6-trihydroxybenzaldehyde	4
5 g *o*-Hydroxyhydroquinone	5 cc	2 Z	..	..	20 g E	2,4,5-trihydroxybenzaldehyde	4
30 g Anisole	30 g	45	40-5	4	..	anisaldehyde (100%)	1 5, 6
25 g Phenetole	25 g	35	40	4	..	*p*-ethoxybenzaldehyde (100%)	1
o-Cresyl methyl ether	..	..	..	..	..	4-methoxy-3-methylbenzaldehyde (90%)	5, 6
o-Cresyl ethyl ether	..	..	..	..	..	4-ethoxy-3-methylbenzaldehyde (95%)	5
m-Cresyl methyl ether	..	..	..	.	..	4-methoxy-2-methylbenzaldehyde (90%)	5
m-Cresyl ethyl ether	..	..	..	..	.	4-ethoxy-2-methylbenzaldehyde	5
p-Cresyl methyl ether	..	..	..	..	B	3-methoxy-6-methoxybenzaldehyde (80%)	1
p-Cresyl ethyl ether	..	..	..	..	B	5-methyl-2-ethoxybenzaldehyde	1
20 g Resorcinol monomethyl ether	20 g	30	35-40	4	40 g B	4-hydroxy-3-methoxybenzaldehyde	2 3
15 g Orcinol monomethyl ether	15 cc	22	room 30-40	4	30 cc B	4-hydroxy-6-methoxy-2-methylbenzaldehyde	1
5 g of *sym*-Xylenyl methyl ether	10 cc	5 Z	..	0 5	30 cc E	2,6-dimethyl-4-methoxybenzaldehyde	1
5 g *sym*-Xylenyl ethyl ether	10 cc	5 Z	..	0 5	30 cc E	2 6-dimethyl-4-ethoxybenzaldehyde	1
vic. m-Xylenyl methyl ether	..	..	..	..	B	4-methoxy-3,5-dimethylbenzaldehyde, but mostly the 4-hydroxy compound	1
vic. m-Xylenyl ethyl ether	..	..	..	..	B	4-ethoxy-3,5-dimethylbenzaldehyde, but mostly the 4-hydroxy compound.	1
17.5 g Diphenyl ether	18 cc	27	0 30-40	3	30 g B	4-phenoxybenzaldehyde (50%)	1
Diphenyl ether	excess	..	..	..	..	4-phenoxybenzaldehyde	14
o,o'-Dimethoxybiphenyl	10 cc	10	0 70	1 2-3	40 g B	2,2'-dimethoxybiphenyldialdehyde-5,5'	1
o,o'-Diethoxybiphenyl	10 cc	10	0 70	1 2-3	40 g B	2,2'-diethoxybiphenyldialdehyde-5,5' (80%)	1
5 g β-Naphthyl methyl ether	7 cc	5	45	2	15 g B	2-methoxynaphthaldehyde-1	1
5 g β-Naphthyl ethyl ether	7 cc	5	45	2	15 g B	2-ethoxynaphthaldehyde-1	1
α-Naphthyl ethyl ether	..	..	..	..	B	4-ethoxynaphthaldehyde-1	1
25 g Veratrole	30 g	25	35-40	7	20 g B	3,4-dimethoxybenzaldehyde (60%)	1
25 g Pyrocatechol diethyl ether	30 g	25	35-40	7	20 g B	3,4-diethoxybenzaldehyde (75%)	1
60 g Resorcinol dimethyl or diethyl ether	80-90 cc	40 g Z	..	..	400 cc E	2,4-dialkoxybenzaldehyde	10
20 g Resorcinol dimethyl ether	20 g	30	0 40-45	4	30 g B	2,4-dimethoxybenzaldehyde	1
20 g Hydroquinone dimethyl ether	15 cc	10	0 35-40	4	18 g B	2,5-dimethoxybenzaldehyde	7
10 g Hydroquinone dimethyl ether	10 cc	15	30	3.5	10 g B	2,5-dimethoxybenzaldehyde	1

Table 31—*(Continued)*

Phenol or Phenol Ether	HCN	Catalyst (g)	Temp. (°C)	Time (hrs)	Solvent	Product	Ref.
10 g Hydroquinone diethyl ether	12 cc	18	30	1	80 g B	2,5-diethoxybenzaldehyde	1
Homopyrocatechol dimethyl ether	..	..	40	..	..	4,5-dimethoxy-2-methylbenzaldehyde	6
15 g Homopyrocatechol dimethyl ether	17 g	25	0 30	1	20 g B	4,5-dimethoxy-2-methylbenzaldehyde (100%)	1
15 g Homopyrocatechol methylethyl ether	17 g	25	0 30	1	20 g B	4-methoxy-5-ethoxy-2-methylbenzaldehyde	1
5 g Hydroxyhydroquinone trimethyl ether	6 cc	5	0 40-50	..	10 g B	2,4,5-trimethoxybenzaldehyde	12
4 g Cresorcinol-dimethyl ether	5 cc	7	..	2	20 g B	2,4-dimethoxy-5-methylbenzaldehyde (100%)	1
20 g Orcinol dimethyl ether	..	30	room 30-40	3	40 cc B	4-hydroxy-6-methoxy-2-methylbenzaldehyde (70%)	1
110 g Pyrogallol trimethyl ether	50 g	90	..	5	110 cc B	2,3,4-trimethoxybenzaldehyde (31-53%)	17, 18
10 g Ethylene glycol diphenyl ether	15 cc	20	0 30-40	24	60 g B	ethylene glycol bis-(4-formylphenyl ether)	1
10 g Trimethylene glycol diphenyl ether	20 cc	20	0 30-40	10 24	60 g B	trimethylene glycol bis-(4-formylphenyl ether) (80%)	1
20 g Ethylene glycol di-*o*-tolyl ether	20 cc	20	10-22	24	60 g B	ethylene glycol bis-(3-methyl-4-formylphenyl ether) (100%)	1
10 g Trimethylene glycol di-*o*-tolyl ether	20 cc	20	0 10-22	24	60 g B	trimethylene glycol bis-(3-methyl-4-formylphenyl ether)	1
10.5 g Ethylene glycol di-*m*-tolyl ether	20 cc	10	0	24	125 g B	ethylene glycol bis-(3-methyl-4-formylphenyl ether) (33%)	1
12 g *m*-Chlorophenol	15 cc	20	−10 30	3	20 g B	2-chloro-4-hydroxybenzaldehyde (50%)	1
30 g *m*-Bromophenol	30 cc	35	40	4	100 g B	2-bromo-4-hydroxybenzaldehyde (10%)	1
30 g *o*-Chloroanisole	30 g	30	30	3	B	3-chloro-4-methoxybenzaldehyde	1
7 g *m*-Chloroanisole	10 cc	11	25	2	30 g B	2-chloro-4-methoxybenzaldehyde	1
15 g *x*-Chlororesorcinol	10 cc	18	0 45	..	50 cc B	*x*-chloro-2,4-hydroxybenzaldehyde	1
15 g *m*-Chlorophenetole	15 cc	25	room	2	40 g B	2-chloro-4-ethoxybenzaldehyde (80%)	1
10 g *m*-Bromophenetole	10 cc	15	−8 30	4	40 g B	2-bromo-4-ethoxybenzaldehyde	1
10 g (β-Bromoethyl) phenyl ether	15 cc	10	0 45	2	50 g B	4-(β-bromoethoxy)benzaldehyde (50%)	1
(β-Bromoethyl)-*o*-cresyl ether	15 cc	10	0 45	2	50 cc B	4-(β-bromoethoxy)-3-methylbenzaldehyde (50%)	1

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1. L. Gattermann, *Ann.*, 357, 313-383 (1907).
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3. L. Gattermann and T. von Horlacher, *Ber.*, 32, 284-286 (1899).
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7. H. Kauffmann and K. Burr, *Ber.*, 40, 2353-2358 (1907).
8. German P. 101,333 to Bayer & Co.; *C. Z.*, 1899 I, 960.
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10. O. Asselmino, *Ber.*, 35, 4099-4108 (1902).
11. German P. 106,508 to Bayer & Co.; *C. Z.*, 1900 I, 742.
12. L. Gattermann and F. Eggers, *Ber.*, 32, 290-291 (1899).
13. J. W. Smith, *J. Chem. Soc.*, 109 I, 70 (1916).

Table 31—*(Concluded)*

14. German P. 650,430 (1937) to K. H. Slotta and K. H. Saurwein (to Chem. Fabrik von Heyden), *C. A.*, 32, 958.
15. T. B. Johnson and F. W. Lane, *J. Am. Chem. Soc.*, 43, 348-355 (1921).
16. C. Liebermann and S. Lindenbaum, *Ber.*, 41, 1607-1619 (1908).
17. F. Schaaf and A. Labouchere, *Helv. Chim. Acta*, 7, 357-363 (1924); *C. A.*, 18, 1838.
18. K. H. Slotta and H. H Heller, *Ber.*, 63, 3029-3044 (1930)
19. G. T. Morgan and D. C. Vining, *J. Chem. Soc*, 119, 177-187 (1921).

chloride was again passed in very slowly while the mixture was heated at 40-45° for three or four hours. Mechanical stirring was used throughout. At the end of the reaction, the imide hydrochlorides had separated out. Hydrolysis was effected with hydrochloric acid, and isolation of the aldehydes either by steam distillation or by salting out and extraction with ether. The following results were reported:

Phenol Ether	Zinc Cyanide (g)	$AlCl_3$ (g)	Benzene (g)	% Yield of Aldehyde
65 g Anisole	52	45	65	100
30 g *p*-Cresol methyl ether	52	45	75	80
25 g Resorcinol dimethyl ether	40	38	100	80
30 g Diphenyl ether	52	45	70	50
30 g *o*-Cresol	52	45	90	38
20 g Thymol	37	30	60	100
30 g *β*-Naphthol methyl ether	52	45	150	100

Gattermann was not able to react benzene with hydrogen cyanide and hydrogen chloride in the presence of aluminum chloride,[32] but a patent [33] appearing just before Gattermann's publication cited the preparation of aldehydes from aromatic hydrocarbons by this method. In 1931, Hinkel and Dunn [34] noted that a complex, $AlCl_3.2HCN$ is formed when hydrogen cyanide is added to a mixture of benzene and aluminum chloride. A few years later, Hinkel and his co-workers [35] found that at its boiling point, benzene reacts with hydrogen cyanide, hydrogen chloride, and aluminum chloride to give benzaldehyde in a 14 per cent of theoretical yield, calculated on the hydrogen cyanide. Yields of 85-100 per cent of aldehyde were secured from toluene, the three xylenes, and mesitylene. Highest yields were obtained at 100° and with aluminum chloride in excess of what is needed to form the compound $AlCl_3 . 2HCN$

Subsequent investigation [36] showed that reaction may be facilitated by the use of the proper solvent; chlorobenzene, dichlorobenzene, and tetrachloroethane were found to be suitable, although chlorobenzene formed 8 per cent *p*-chlorobenzaldehyde, and tetrachlorethane promoted polymerization and condensation in some cases, notably with indene. The technique consisted in adding the hydrocarbon to the $AlCl_3 . 2HCN$ in a solvent, and then passing hydrogen chloride through the mixture. Using this technique, aldehyde derivatives of the following hydrocarbons were prepared in the indicated yields:

[32] L. Gattermann and C. Frensel, *Ber.*, 31, 1149-1152 (1898).
[33] German P. 99,568 to Bayer & Co.
[34] L. E. Hinkel and E. T. Dunn, *J. Chem. Soc.*, 1834-1839 (1930).
[35] L. E. Hinkel, E. E. Ayling, and W. H. Morgan, *J. Chem. Soc.*, 2793-2796 (1932); *cf.* Brit P 367,124 (1932) to L. E. Hinkel (to Imperial Chemical Industries), *Brit. Chem. Abs.*-B, 906 (1933)
[36] L. E. Hinkle, E. E. Ayling, and J. H. Beynon, *J. Chem. Soc.*, 339-348 (1936).

Mesitylene	
Biphenyl	75%
Naphthalene	60%
1-Methylnaphthalene	51%
1,6-Dimethylnaphthalene	58%
Tetralin	4% to resin
Hydrindene	45%
Anthracene	60%
Phenanthrene	44%
Acenaphthene	70%
Fluorene	

At about the same time, Robinson and Thompson [37] reported that, in an attempt to prepare 1-methyl-4-naphthaldehyde from α-methylnaphthalene by condensing it with hydrogen cyanide and hydrogen chloride in the presence of aluminum chloride, a poor yield of the aldehyde, which was isolated as the semicarbazone (m.p. 237°) was secured. These investigators do not give the temperature at which reaction was conducted.

When ethereal solutions of bimolecular hydrogen cyanide are saturated with hydrogen chloride, chloromethyleneformamidine, 2HCN.HCl, is precipitated as a white solid. The chloro- compound reacts with benzene in the presence of aluminum chloride to yield benzaldehyde.[34]

In tetrachloroethane solution, the following results were secured [36]:

Hydrocarbon	$(HCN)_2HCl$ (mols.)	$AlCl_3$ (mols.)	Reaction: Time min.	Reaction: Temp. (°C)	% Yield of Aldehyde
Benzene	2.5	4.0	65	5	75
Naphthalene	2.0	0.5	70	4	66
Anthracene	2.0	2.0	50	3	50
Hydrindene	2.0	0.5	50	4	60
Acenaphthene	1.0	2.0	50	1.5	90
Fluorene	1.25	1.25	50	4	70

Biphenyl gave a mono-aldehyde in chlorobenzene or *o*-dichlorobenzene solution, but in tetrachloroethane solution, only small yields of the *p,p'*-dialdehyde were secured.

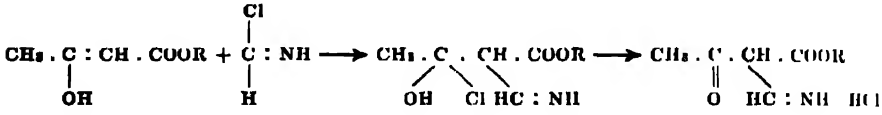
Since the Gattermann aldehyde synthesis with aromatic hydrocarbons is possible only at temperatures above 40°, at which temperature the complex $AlCl_3.2HCN$ is decomposed, and since chloromethyleneformamidine reacts with aromatic hydrocarbons in the presence of aluminum chloride to give good yields of aldehydes, it is probable that the Gattermann aldehyde synthesis with aromatic hydrocarbons proceeds through primary formation of $AlCl_3.2HCN$, and intermediate formation of chloromethyleneformamidine from hydrogen chloride and the hydrogen cyanide formed by decomposition of the complex.

An attempt to extend the Gattermann reaction to olefinic compounds using hydrogen chloride and hydrogen cyanide in the presence of aluminum chloride was relatively unsuccessful due to the powerful polymerizing action of aluminum chloride on such compounds.[38] Thus *asym*-diphenylethylene was 30 per cent polymerized to 1,1,3,3-tetraphenylcyclo-

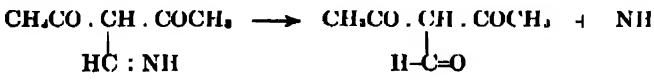
[37] R. Robinson and H. W. Thompson, *J. Chem. Soc.*, 2015-2019 (1932).
[38] H. Wieland and E. Dorrer, *Ber.*, 63, 404-411 (1930).

butane and some α,α-diphenylpropionitrile was also formed. Styrene polymerized rapidly to polystyrene.

Wieland and Dorrer [39] studied this synthesis with enols and observed that acetoacetic ester reacted with hydrogen cyanide and hydrogen chloride in the presence of aluminum chloride, much the same as do phenols. Only the enol form reacted in spite of the presence of 90 per cent in the keto- form. The reaction yielded the hydrochloride of α-formiminoacetoacetic ester.



Acetylacetone reacts analogously, yielding forminoacetylacetone, which is readily hydrolyzed:



It should be noted that imines formed in these syntheses show both acid and basic properties, forming enol salts with bases and crystalline hydrochloride salts.

The synthesis of aldehydes of the furan series proceeds regularly by the Gattermann method. The following table shows some of the derivatives of this series which have been prepared.

Reactant	Product	Reference
Furan	furfural	1
α-Methylfuran	5-methylfurfural	1
β-Methylfuran	3-methylfurfural	2
α-Ethylfuran	5-ethylfurfural	1
2,4-Dimethylfuran	3,5-dimethylfurfural	2
Difurylethane	difurylethane-5,5'-dialdehyde	1
Dibenzofuran	dibenzofuran-3-aldehyde	3

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1. T. Reichstein, *Helv. Chim. Acta*, 13, 345-349 (1930).
2. T. Reichstein, H. Zschokke, and A. Georg, *Helv. Chim. Acta*, 14, 1277-1283 (1931).
3. L. E. Hinkel, E. E. Ayling, and J. H. Beynon, *J. Chem. Soc.*, 775-780 (1937).

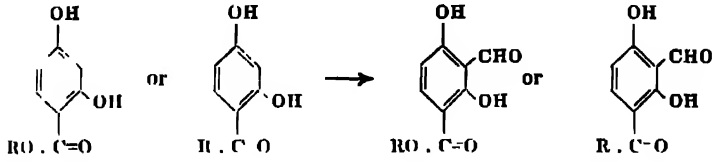
Reichstein [40] has compared the susceptibility of the three simplest five-membered heterocyclic compounds to the Gattermann reaction. He found that in the absence of a catalyst pyrrole would react almost regardless of other constituents of the ring; furan was somewhat less reactive but would react except when both α-positions were occupied or when a carboxylate or a phenylene group replaced an H in the ring. Thiophene would not react unless aluminum chloride were present.

A reaction which is related to the Gattermann aldehyde synthesis involves the use of formamide with aluminum chloride on oxygenated

[39] H. Wieland and E. Dorrer, *Ber.*, 55, 815-820 (1925).
[40] T. Reichstein, *Helv. Chim. Acta*, 13, 349-356 (1930).

cyclic compounds for the introduction of the aldehyde group.[41] Thus β-naphthol treated with a large excess of formamide mixed with aluminum chloride and heated to 130-140° produces 2-naphthol-1-aldehyde.

The Gattermann aldehyde synthesis has been recently applied by Shah and his co-workers to resorcinol esters, acids, and ketones. Substitution occurs at the 2-position, which is highly activated by the chelation between the hydroxy and the carbonyl groups:



The condensation was effected by passing hydrogen chloride into a solution of one mole of the resorcinol derivative, 2 moles of zinc cyanide, and 2 moles of aluminum chloride in dry ether. Aldehydes were prepared from methyl β-resorcylate,[42] methyl 2,4-dihydroxy-5-ethylbenzoate,[43] resacetophenone, respropiophenone, resbutyrophenone,[44] β-resorcinolic acid,[45] 2,4-dihydroxy-4-ethylacetophenone, 6-methylresacetophenone, 2-acetylresorcinol, phloroacetophenone, and 2-hydroxy-6-methoxyacetophenone.[46]

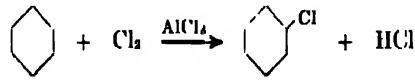
[41] German P. 519,806 (1928) to I. G.; *C. A.*, 25, 3012; Brit. P. 311,208 (1928) to A. Carpmael (to I. G.), *Brit. Chem. Abs.*-B, 747 (1929).
[42] R. C. Shah and M. C. Laiwalla, *Current Sci.*, 5, 197-198 (1936); *J. Chem. Soc.*, 1828-1832 (1938).
[43] H. A. Shah and R. C. Shah, *J. Chem. Soc.*, 300-302 (1939).
[44] H. A. Shah and R. C. Shah, *J. Chem. Soc.*, 132-134 (1939); *ibid*; 245-247 (1940).
[45] K. Nakazawa, *J. Pharm. Soc. Japan*, 59, 169-176 (1939); *C. A.*, 33, 4978.
[46] K. Nakazawa, *J. Pharm. Soc. Japan*, 59, 524-30 (in German, 199-202) (1939), *C. A.*, 34, 1017.

Chapter 11

Aromatic Halogenation

The halogenation of a wide variety of aromatic compounds proceeds readily in the presence of aluminum chloride. This chapter describes the application of these processes.

Anhydrous aluminum chloride, like ferric chloride, catalyzes nuclear halogenation of aromatic compounds. The reaction, which may be effected in the presence of as little as 0.01 mole of aluminum chloride, proceeds according to the equation



The extent of halogenation is, of course, regulated by the amount of halogenating agent used and by reaction conditions. Alkylated benzenes, phenols, phenol ethers, and polynuclear hydrocarbons undergo similar reaction.

For aromatic chlorinations effected with sulfuryl chloride or with sulfur monochloride, aluminum chloride is an especially effective catalyst. With alkylbenzenes, side-chain substitution is entirely inhibited. Thionyl chloride ordinarily cannot be used as the chlorinating agent, yielding, in most instances, normal Friedel-Crafts reaction products. However, it has been used for chlorination of certain dicarboxylic acids and for the conversion of alkyl ethers into alkyl halides.

Carbon tetrachloride or benzotrichloride are other halogenating agents which have been used in the presence of aluminum chloride. Bromination may be conveniently effected by transfer of bromine from one nucleus to another.

The use of aluminum chloride as a catalyst in the halogenation of aliphatic compounds is discussed in the chapter on aliphatic reactions.*

Reactions with Halogens

The chlorination of benzene proceeds readily with the formation of practically all the possible products depending upon the amount of chlorine added.[1] One mole of chlorine with benzene gives mainly chlorobenzene with a small amount of the three dichlorobenzenes and some unchanged hydrocarbon. Monochlorobenzene forms all three dichlorobenzenes with the *para*- isomer predominating, whereas ferric chloride

* See Chapter 17.

[1] A. Mouneyrat and Ch. Pouret, *Compt. rend.*, 127, 1025-1027 (1898); *J. Chem. Soc. Abs.*, 76 I, 263. A. Korczynski, *Bull. soc. chim.*, 29, 233-240 (1921), *C. A.*, 15, 2018.

favors *ortho-* chlorination. With bromination the reverse is true. Further chlorination will yield three trichlorobenzenes, tetrachloro-, pentachloro-, and hexachlorobenzene. Results are not always consistent because of the aluminum chloride splitting off chlorine to regenerate the hydrocarbon. Iodine as a catalyst favors *ortho-* and *para*-dichlorobenzene.[2] Chlorination and bromination of bromobenzene also favor the formation of the *para-* isomer although bromination gives much *meta*-derivative. Bromination of benzene proceeds in an analogous manner, with the formation of mono-, di-, and tribromobenzenes.[3]

In an industrial process for the manufacture of chlorobenzene, to be used in the synthesis of phenol, chlorination of benzene is effected by using a catalyst composed of activated aluminum chloride in combination with copper salts.[4]

A Raman spectra study of the bromination of benzene or chlorobenzene in the presence of aluminum chloride shows the formation of the three dibromobenzenes, although the use of beryllium bromide as a catalyst gave only *ortho-* and *para-* derivatives.[5]

The chlorination of *m*-dichlorobenzene gives mainly 1,2,4-trichlorobenzene.[6]

A method of separating ethylbenzene from the xylenes is offered by the action of bromine with 1 per cent iodine on these compounds in the presence of aluminum chloride.[7] The xylenes are completely converted to the tetrabromo- derivatives, and ethylbenzene forms a dibromoethylbenzene. Bromination of naphthalene in the presence of aluminum chloride always produces the alpha derivative.[8] Naphthalene may be rapidly and exhaustively chlorinated to octachloronaphthalene by treatment with chlorine in the presence of an active halogen carrier such as aluminum chloride. In the absence of the halogen carrier the rate is much slower.[9]

Seven to ten atoms of chlorine have been introduced into perylene by chlorinating in nitrobenzene using aluminum chloride as a catalyst. A temperature of 100-140° was used.[10] Hepta- to dodecachloroperylene may be prepared from a chloroperylene containing less than seven chlorine atoms.[11]

Under certain conditions aluminum chloride is able to chlorinate perylene by itself, although not below 150°C. When nitrobenzene is present as an oxidizing agent, aluminum chloride converts perylene to 4,10-di-

[2] A. F. Holleman and T. van der Linden, *Rec. trav. chim.*, 30, 305-330 (1911); *J. Chem. Soc. Abs.*, 102 (I), 20 (1912).
[3] A. J. Leroy, *Bull. soc. chim. (2)*, 48, 210-16 (1887); *J. Chem. Soc. Abs.*, 54, 258 (1888).
[4] W. Mattes, *Angew. Chem.*, 52, 501 (1939).
[5] R. Pajeau, *Compt. rend.*, 207, 344-345 (1938); *C. A.*, 32, 8379.
[6] S. C. J. Olivier, *Rec. trav. chim.*, 39, 411-413 (1920); *J. Chem. Soc. Abs.*, 118 (I), 478 (1920). J. B. Cohen and P. Hartley, *J. Chem. Soc.*, 87, 1360-1367 (1905).
[7] C. Friedel and J. M. Crafts, *Compt. rend.*, 101, 1218-1223 (1885); *J. Chem. Soc. Abs.*, 50, 230 (86).
[8] L. Roux, *Bull. soc. chim. (3)*, 45, 510-521 (1886); *J. Chem. Soc. Abs.*, 50, 806 (1886).
[9] V. Shvemberger and V. Gordon, *J. Gen. Chem. (U. S. S. R.)*, 4, 529-551 (1934); *C. A.*, 29, 1804.
[10] British P. 288,171 (1928) to F. Bensa; *Brit. Chem. Abs.*-B, 921 (1928).
[11] U. S. P. 1,712,862 (1929), French P. 651,658 (1928) to A. Zinke and K. Funke (to F. Bensa); *C. A.*, 23, 3383.

chloroperylene, and with the addition of manganese dioxide 3,4,9,10 tetrachloroperylene is formed.[12]

Phenol or chlorophenols may be converted to pentachlorophenol by using 0.01 to 0.04 mole of aluminum chloride per mole of phenol as a catalyst.[13]

In another method, tetra- or pentahalogenated phenols are prepared by reaction of phenol or lower halogenated phenols with chlorine in the presence of halogen carriers at below 50°. Inert solvents, like carbon tetrachloride or ethylene chloride, are specified.[14]

Halogen derivatives of phenol have also been prepared by progressively adding to the phenol, in presence of a catalyst like aluminum chloride, an amount of halogen slightly in excess of that required, while agitating and separating the halogen derivative formed. Chloroform may be used as solvent, and the product may be extracted by a solvent. The process has been applied to preparation of di- or tribromo derivatives of xylenols, cumenol, and guiacol.[15]

Diphenyl oxide may be halogenated in the presence of aluminum chloride to yield products containing from 5 to 10 halogen atoms which are useful as heat transfer media or insulating materials.[16]

A study of the catalytic chlorination of nitrobenzene indicated that the rate of reaction is proportional to the catalyst concentration, but for a given quantity of catalyst the chlorination follows the course of a unimolecular reaction The rate with aluminum chloride as catalyst is thirty-one times that of stannic chloride. Ferric chloride is even more effective.[17]

All the chloro-derivatives of phenyl carbonate may be prepared by the chlorination of phenyl carbonate in the presence of a catalyst such as aluminum chloride, iodine, antimony pentachloride, or ferric chloride.[18]

Dyestuffs may be prepared by halogenation in the presence of a sodium or potassium chloride-aluminum chloride melt as catalyst. Thus, halogenated dibenzpyrenequinones are formed by chlorination or bromination of the product obtained by condensing benzoylbenzanthrone or dibenzoylnaphthalene derivatives without isolating the primary product.[19] *n*-Anthraquinonylisatins may be similarly converted into halogenated anthraquinone acridones.[20] Phthalocyanine dyes as green pigments are formed by adding at least eight halogen atoms to a phthalocyanine with aluminum chloride as a halogen carrier.[21]

An instance of preferential aliphatic halogenation is the production

[12] A. Zinke, K. Funke, and N. Lorber, *Ber.*, 60, 577-581 (1927)
[13] U. S. P. 2,121,259 to W. C. Stoesser (to Dow Chemical Co.) *C. A.*, 32, 6102
[14] German P. 557,393 (1931) to R Michel and H Buschmann (to I. G. Farbenind.); *C Z*, 1931, II 2788.
[15] French P. 701,514 (1930) to L. B Palfray and T. M. E Duboc; *C. A.*, 25, 4011.
[16] U. S. P 2,022,634 (1935) to E. C Britton, W. C. Stoesser, and G. G. Goergen (to Dow Chem Co.); *Brit. Chem. Abs.*-B, 1195 (1936)
[17] H. Goldschmidt and H. Larsen, *Z. Physik. Chem.*, 48, 424-434 (1904); *J. Chem Soc. Abs.*, 86 (II) 609 (1904).
[18] E. Barral, *Compt. rend.*, 138, 909-911 (1904); *J. Chem. Soc. Abs.*, 86 (I), 493 (1904)
[19] British P. 338,747 (1929) to I. G.; *Brit. Chem. Abs.*-B, 290 (1931).
[20] British P. 346,350 (1929) to I. G.; *Brit. Chem. Abs.*-B, 968 (1931).
[21] British P. 461,393 (1937) to R. P. Linstead, C. E. Dent, and Imperial Chemical Industries *C A*, 31, 4830.

of ω-bromoacetophenone in 64-66 per cent yield [22] by treating acetophenone in diethyl ether solution with bromine in the presence of aluminum chloride as catalyst.

Halogenation with Compounds of Halogen

Instead of chlorine, chlorine compounds of sulfur are useful as halogenating agents. The chlorinating action of sulfuryl chloride has been explained by Ruff,[23] who observed that aluminum chloride and sulfuryl chloride undergo a reversible reaction at temperatures up to 120°

$$AlCl_3 + SO_2Cl_2 \rightleftharpoons AlCl_3 . SO_2 + Cl_2$$

which will liberate free chlorine for subsequent chlorinations of organic compounds.

In an extended study by Silberrad of the use of sulfuryl chloride as a chlorinating agent for aromatic hydrocarbons, it was found that aluminum chloride is an extremely efficient catalyst. The efficiency of various catalysts [24] for chlorinating benzene is shown in the following summary:

Iodine	16.8%
Thionyl chloride	24%
Sulfur	37%
Sulfur mono chloride	37%
Ferric chloride	53%
Aluminum chloride	
Aluminum chloride with thionyl chloride	83% (dichlorobenzene also formed)
Aluminum chloride with sulfur	89% (dichlorobenzene also formed)
Aluminum chloride with sulfur mono chloride	87% (dichlorobenzene also formed)

The formation of polychloro-derivatives of benzene, di-, tetra-, and hexachlorobenzenes, is brought about by a mixture of sulfuryl chloride, sulfur monochloride, and aluminum chloride.[25] The mixture produces the associated compound, $Al_2S_2Cl_8$, which is reported to have remarkable catalytic property for the higher degree of chlorination of benzene with sulfuryl chloride.

The chlorination of toluene may occur in the ring or in the side chain. Phosphorus pentachloride, manganese chloride, and arsenic chloride as catalysts inhibit substitution in the ring, the manganese and arsenic chloride catalysts being entirely inhibiting. Of the other catalysts studied, aluminum chloride accelerated chlorination in the ring, entirely inhibiting chlorination in the side chain. For polychlorination of toluene Silberrad [26] used the same mixed catalyst, aluminum chloride with sulfur monochloride, as was used to polychlorinate benzene. The production of almost theoretical yields of mono-, di-, and trichlorotoluene, entirely ring-substituted, may be obtained by the addition of definite proportions of

[22] R. M. Cowper and L. H. Davidson, *Organic Syntheses*, 19, 24-26 (1939); *C. A.*, 33, 5379.
[23] O. Ruff, *Chem. Ztg.*, 30, 1225 (1906); *C. Z.*, 1907 I, 148.
[24] O. Silberrad, *J. Chem. Soc.*, 119, 2029-2036 (1921); *C. A.*, 16, 915.
[25] O. Silberrad, *J. Chem. Soc.*, 121, 1015-1022 (1922).
[26] O. Silberrad, *J. Chem. Soc.*, 127, 2677-2684 (1925); *Brit. Chem. Abs.*-A, 158 (1926).

sulfuryl chloride and toluene. Patents covering the use of these catalysts for the control of the chlorination of aromatic hydrocarbons by sulfuryl chloride have been issued.[27]

Alkyl ethers may be converted to alkyl halides by reaction with thionyl chloride using aluminum chloride as a catalyst. With *n*-propyl and *n*-butyl ethers the aluminum chloride also caused isomerization to iso-, secondary, and tertiary halides.[28]

Thionyl chloride reacts with aromatic hydrocarbons in the presence of aluminum chloride to yield sulfoxides. Hence, it is not as generally useful a chlorinating agent as is sulfuryl chloride.[29]

The production of aromatic acid chlorides from aromatic carboxylic acids containing a negative substituent in the position *para*- to the carboxylic group can be accomplished by using thionyl chloride as the halogenating agent in the presence of aluminum chloride as catalyst. Compounds prepared in this manner are: terephthaloyl dichloride, chloroterephthaloyl dichloride, 1,4-naphthalene dicarboxylic dichloride, and 4,4'-biphenyl dicarboxylic dichloride.[30] *o*-Dicarboxylic acid chlorides of the benzene series have also been prepared by treating the corresponding acid anhydrides with thionyl chloride at above the melting point of the anhydride, in the presence of a metal salt of acid reaction.[31]

In connection with the halogenation of aromatic compounds it has been pointed out in the section on halogen migration (pp. 692-696) that some brominated aromatic compounds act as brominating agents in the presence of aluminum chloride as catalyst. For example:

(1) Bromobenzene was prepared from benzene by brominating with bromonaphthalene, tribromophenol, bromochlorophenol, tetrabromocresol, or tribromocresol.

(2) Monobromotoluene was prepared from toluene by brominating with the same brominating agents.

(3) Tribromophenol was prepared by brominating phenol with dibromobenzene.

Paraffinic hydrocarbons having a polychloro-substituted carbon atom yield their halogen when heated with acid anhydrides like phthalic anhydride and aluminum chloride at 250-280°. Phthaloyl chloride has been prepared in this manner from phthalic anhydride and carbon tetrachloride.[32]

o-Dicarboxylic acid chlorides of the benzene series have also been prepared by heating the corresponding acid anhydride in the liquid phase with benzotrichloride, its homologs or its chlorine substitution products in the presence of a catalyst of the Friedel-Crafts type.[33] Similarly,

[27] Brit. P. 188,200 (1921) to A. Boake and O. Silberrad (to Roberts & Co., Ltd.); *C. A.*, 17, 3344 (1923). Brit. P. 250,329 (1925) to O. Silberrad and A. Boake (to Roberts & Co., Ltd.), *Brit. Chem Abs.*-B, 1020 (1926).

[28] Ya. L. Goldfarb and L. M. Smorgonskii, *Bull. acad. sci. U. R. S. S., Classe sci. math nat., Sér. chim.*, 553-561 (1936); *C. A.*, 31, 6613.

[29] A. Schönberg, *Ber.*, 56, 2275 (1923).

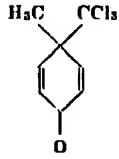
[30] French P. 810,595 (1937) to I. G. Farbenind; *C. A.*, 32, 592

[31] Brit. P. 414,572 (1934) to Monsanto Chemical Co.; *C. A.*, 29, 478.

[32] U. S. P. 2,051,988 (1936) to J. R. Mares (to Monsanto Chemical Co.); *C. A.*, 30, 6763.

reaction of phthalic acid with benzotrichloride at 200° in the presence of aluminum chloride yields phthaloyl chloride.[34]

3,5-Dichloro-*p*-cresol treated with bromine, carbon tetrachloride, and aluminum chloride produces 3,5-dichloro-2,6-dibromo-*p*-cresol and 3,5,-dichloro-2,6-dibromo-*p*-cresol carbonate. However from *p*-cresol, carbon tetrachloride and aluminum chloride, 1-methyl-1-trichloromethyl-4-keto-dihydrobenzene is obtained.[35]



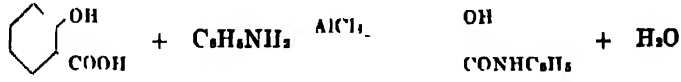
[33] U. S. P. 1,967,749 (1934) to L. P. Kyrides (to Monsanto Chemical Co.); *C. A.*, **28**, 5079; Brit. P. 414,570 (1933) to Monsanto Chemical Co.; *British Chem. Abs.*-B, 875 (1934).
[34] U. S. P. 1,967,748 (1934) to L. P. Kyrides (to Monsanto Chemical Co.); *C. A.*, **28**, 5080.
[35] T. Zincke and R. S. Suhl, *Ber.*, **39**, 4148-4153 (1906); *C. A.*, **1**, 569.

Chapter 12

Dehydrating Reactions

The first part of this chapter deals with the use of alcohols for the alkylation of aromatic compounds in the presence of aluminum chloride The mechanism of such reactions necessarily involves a study of the reaction of alcohols alone with aluminum chloride There is some evidence that the first step in these alkylating reactions is the formation of the chloride from the alcohol and that this derivative acts as the alkylating agent; however, the fact that alkylation of benzene with *n*-propyl alcohol yields *n*-propylbenzene contradicts such a mechanism Aliphatic, aralkyl, and cycloalkyl alcohols and their chlorinated or oxygenated derivatives have been studied as alkylating agents.

The replacement of oxygen from carbonyl groups is also reviewed in this chapter. This includes such reactions as ketones with amines in which the oxygen in the —C=O group and hydrogen of the amino group are removed as water. The carboxylic group of acids may be similarly affected. Thus salicylic acid and aniline forms salicylanilide.



Autocondensation of ketones and the intramolecular ring closure of carboxylic acids also occurs, with loss of water in the presence of aluminum chloride. This includes such reactions as the conversions of acetophenone to 1,3,5-triphenylbenzene and ring closure of aroylbenzoic acids

Aliphatic aldehydes and aromatic compounds condense in the presence of aluminum chloride with elimination of water. Reactions of formaldehyde with aromatic hydrocarbons may give rise to a series of arylated paraffins, whereas under similar conditions aromatic halides may yield resins. Aromatic aldehydes with aromatic hydrocarbons yield polynuclear compounds. Chloromethyl derivatives of hydrocarbons may be prepared by reaction with formaldehyde and hydrogen chloride in the presence of a mixture of aluminum chloride and zinc chloride.

A few miscellaneous reactions in which water is eliminated during reaction are included at the end of the chapter.

Alkylation with Alcohols, Aromatic Hydrocarbons or Their Halogen Derivatives

The condensation of alcohols with aromatic hydrocarbons in the presence of aluminum chloride results in alkylation of the hydrocarbon with

water-cleavage. The reactivity of aliphatic alcohols increases in the order: primary, secondary, tertiary. Earlier workers reported that primary alcohols could not be caused to react with benzene, that secondary alcohols showed little reactivity, and that tertiary alcohols only gave good results. Subsequent investigation of this reaction revealed that all three types of alcohols undergo the reaction, but that primary and secondary alcohols require the presence of excess of catalyst and longer heating.

Previous to the publication of this work, much work had been done on comparison of various aliphatic and aralkyl alcohols as Friedel-Crafts alkylating agents. These investigations are of inestimable value in revealing the influence of structure on chemical reactivity.

The condensation of aliphatic alcohols with aromatic hydrocarbons in the presence of aluminum chloride has been shown to be favored by unsaturation of the α-carbon atom of the alcohol. In a series of studies on this reaction, Huston and his co-workers have found that the unsaturation may be due to an aromatic ring,[1] to a simple double bond,[2] or a strain in a polymethylene ring.[3] Reactivity of certain aralkyl or cycloalkyl alcohols is greater than that of aliphatic alcohols.

Aliphatic Alcohols: Primary

Norris and his co-workers [4] have found that the course of the reaction of alcohols with aromatic hydrocarbons is definitely regulated by the quantity of aluminum chloride employed.[5] It had been previously shown [6] that in the Friedel-Crafts condensation of aliphatic anhydrides with aromatic compounds good results are secured only when sufficient catalyst is used to convert the anhydride into an acid halide-aluminum chloride complex. That condensations with alcohols similarly proceed through formation of halides may be assumed from the fact that with primary alcohols alkylated products are secured only when the catalyst is present in excess. According to Norris and Sturgis [4] one mole of alcohol reacts with one mole of aluminum chloride to give the corresponding alkyl halide. With ethyl alcohol the following reaction occurs:

$$C_2H_5OH + AlCl_3 \longrightarrow C_2H_5OH \,.\, AlCl_3 \longrightarrow$$
$$HCl + C_2H_5O \,.\, AlCl_2 \longrightarrow C_2H_5Cl \text{ and } AlOCl$$

The addition product, $C_2H_5OH.AlCl_3$, was formed at room temperature. Upon heating, a nearly quantitative yield of ethyl chloride was secured. Methyl alcohol was found to react analogously, and isopropyl alcohol gave 70 per cent isopropyl chloride. The transformation of the alcohols to the corresponding alkyl halides by reaction with the catalyst obvi-

[1] R. C. Huston and T. E. Friedemann, *J. Am. Chem. Soc.*, 38, 2527-2533 (1916); *ibid.*, 40, 785-793 (1918); R. C. Huston, *ibid.*, 46, 2775-2779 (1924).
[2] R. C. Huston and D. D. Sager, *J. Am. Chem. Soc.*, 48, 1955-1959 (1926).
[3] R. C. Huston and K. Goodemoot, *J. Am. Chem. Soc.*, 56, 2432-2434 (1934).
[4] J. F. Norris and J. N. Ingraham, *J. Am. Chem. Soc.*, 60, 1421-1423 (1938). J. F. Norris and D. M. Sturgis, *ibid.*, 61, 1413-1417 (1939).
[5] *cf.* J. F. Norris and D. Rubinstein, *ibid.*, 61, 1163-1170 (1939) for the effect of molar ratio of reactants on alkylation with alkyl halides.
[6] P. H. Groggins and R. H. Nagel, *Ind. Eng. Chem.*, 26, 1313-1316 (1934). P. H. Groggins, R. H. Nagel, and A. J. Stirton, *ibid.*, 26, 1317-1318 (1934); *cf.* also p. 000 and p. 000 in which it is shown that in alkylations with ethers or esters there is a preliminary formation of halogen derivatives.

ously indicates the need of more than one mole of aluminum chloride in order that further reaction of the resulting alkyl halide with an aromatic compound may be effected. The fact that alkylation with alcohols does not proceed simply through formation of the complex $RO.AlCl_2$ was illustrated with ethyl alcohol. The compound $C_2H_5O.AlCl_2$ was prepared by heating molecular quantities of ethyl alcohol and aluminum chloride until evolution of hydrogen chloride had ceased. Heating this complex with benzene at 90° for four hours gave no ethyl derivatives of benzene.

Observations concerning the mechanism of the reaction had previously been made by other investigators. According to Perrier and Pouget [7] and Mpetse [8] the action of aluminum chloride on a primary alcohol varies with the quantity of the salt which is present and the temperature used. If the alcohol is in excess, and reaction is effected in the cold, compounds of the type $Al_2Cl_6(ROH)_n$ are formed. If the aluminum chloride is in excess, and heating is employed, liberation of hydrogen chloride ensues, with formation of addition compounds of the type $Al_2Cl_4(OR)_2$. The following reaction also takes place:

$$AlCl_2(OR) + ROH \qquad ROR + AlCl_2(OH)$$

The foregoing sequence of condensations has been assumed by Tzukervanik [9] to be accompanied also by dehydrohalogenation and hydrohalogenation, if an excess of aluminum chloride and heating are employed This investigator advances the following scheme for the action of aluminum chloride on amyl alcohol:

$$C_5H_{11}OH + AlCl_3 \longrightarrow AlCl_2.O.C_5H_{11} + HCl$$
$$AlCl_2.O.C_5H_{11} \longrightarrow C_5H_{10} + AlCl_2.OH$$
$$C_5H_{10} + HCl \longrightarrow C_5H_{11}Cl$$

Such a series of reactions as primary steps in the condensation of alcohols with aromatic hydrocarbons in presence of aluminum chloride indicates the presence not only of an alkyl halide, but also of an olefin, hydrogen chloride, and aluminum chloride addition products, all of which are required for Friedel-Crafts alkylation with alkyl halides or olefinic hydrocarbons.

Although various investigators [10] have attempted without success the methylation of benzene with methanol in presence of aluminum chloride, Norris and Sturgis have effected the reaction by using a large excess of aluminum chloride. They report that when benzene, methanol, and aluminum chloride in a 4:1:1 molar ratio are heated at 80-90° for eight hours, and then at 100° for six hours, no methylbenzenes are formed, although hydrogen chloride is evolved. When the above-mentioned reactants are used in a 6:1:2 molar ratio, however, and the mixture is

[7] G. Perrier and I. Pouget, *Bull. soc. chim. (3)*, **25**, 551-556 (1901), *J. Chem. Soc. Abs.*, **80** (I), 442 (1901).
[8] St. K. Mpetse, *Praktika*, **6**, 148-153 (1931); *C. Z.*, 1931 II, 1601.
[9] I. Tsukervanik, *J. Gen. Chem. (U. S. S. R.)*, **5**, 117-120 (1935).
[10] R. C. Huston and T. Y. Hseh, *J. Am. Chem. Soc.*, **53**, 439-441 (1936). I. P. Tsukervanik and G. Vikhrova, *J. Gen. Chem., U. S. S. R.*, **7**, 833-836 (1937); *C. A.*, **31**, 5770.

heated for three hours at 90° and six hours at 90-96°, a 21 per cent of theoretical yield of toluene is secured.

Condensation of toluene with methanol, effected by heating a mixture consisting of 2 moles of aluminum chloride, 2.5 moles of toluene, and 1 mole of methanol for 3½ hours at 100° while a stream of dry air was passed through it, gives a 53 per cent yield of mesitylene.[4] When 1 mole of *m*-xylene is reacted with 1 mole of methanol in presence of 3 moles of aluminum chloride, somewhat higher yields of mesitylene were secured.[11]

Condensation of ethanol with benzene likewise depends upon the amount of catalyst used.[4] With ethyl alcohol, benzene and aluminum chloride in a 1:6:2 molecular ratio, a 50 per cent of theoretical yield of ethylbenzene can be secured. Reaction was effected by allowing a mixture consisting of 0.5 mole of ethyl alcohol, 3 moles of benzene, and 1 mole of aluminum chloride to stand over night, and then heating at 100° for 12 hours.

The accelerating effect of excess of catalyst and higher temperatures had been previously pointed out by Tsukervanik and Vikhrova.[12] These investigators reported the following reactions:

Hydrocarbon	Alcohol	$AlCl_3$ (g)	Reaction temp. (°C)	Hours of heating	Product
120 g benzene	16 g ethyl	87	120–130	10	48.5% ethylbenzene and 35% of polyalkylbenzene
120 g benzene	30 g propyl	87	110	10	51.5% propylbenzene and 36.5% *m*-dipropylbenzene
g toluene	23 g ethyl	99	140	8	74% *m*-ethyltoluene and 20% diethyltoluene
80 g toluene	30 g propyl	90	125	4	83% of *m*- and *p*-propyltoluene and 9.5% of dipropyltoluene

In the foregoing condensations 1.3 to 2 moles of aluminum chloride were used for 1 mole of alcohol. The reaction of ethyl alcohol with benzene also yielded some diethylbiphenyl and diethyltriphenyl. Contrary to the results of Norris and Sturgis[4] condensation could not be effected with methyl alcohol and benzene; with toluene, alkyl derivatives of various degrees of alkylation were secured.

Huston and Hsieh[10] have found that primary alcohols up to and including *n*-hexyl alcohol do not react with benzene when one equivalent of the alcohol is gradually added to a suspension of 0.5 equivalent of aluminum chloride in 2 to 5 equivalents of benzene at low temperature.

Ipatieff and his co-workers[13] have pointed out that since alkylation of benzene with *n*-propyl alcohol in the presence of aluminum chloride

[11] J. F. Norris and J. N. Ingraham, *J. Am. Chem. Soc.*, **60**, 1421-1423 (1938).
[12] I. P. Tsukervanik and G. Vikhrova, *J. Gen. Chem. U. S. S. R.*, **7**, 632-636 (1937); *C. A.*, **31**, 5770.
[13] V. N. Ipatieff, H. Pines, and L. Schmerling, *J. Org. Chem.*, **5**, 253-263 (1940). cf. H. Pines, L. Schmerling, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **62**, 2901-2 (1940), for reaction of neopentyl alcohol with benzene and $AlCl_3$ to give the unrearranged product, neopentylbenzene.

results in production of *n*-propylbenzene in 26 per cent yield, the reaction cannot proceed through intermediate formation of an alkyl halide, for in that case the product would be isopropylbenzene.

Olefinic Primary Aliphatic Alcohols.—That a simple double bond has an activating effect on Friedel-Crafts alkylation with alcohols is indicated in the condensation of allyl alcohol with benzene, effected by treating a mixture of 1 mole of the alcohol and 5 moles of benzene with 0.5 mole of aluminum chloride at room temperature. Allylbenzene was obtained in only 16 per cent yield, probably because of a side reaction involving the aluminum chloride-catalyzed addition of hydrogen chloride to the double bond of the alcohol.[14]

The condensation of an aliphatic unsaturated alcohol, such as oleyl alcohol, with benzene in the presence of aluminum chloride and subsequent sulfonation of the product results in production of a washing agent.[15]

Halogenated Primary Alcohols.—The condensation of β-chloroethyl alcohol with benzene and aluminum chloride at 100° but not at 50-60° gives bibenzyl in 38.9 per cent yield [16]:

$$ClCH_2.CH_2OH + 2C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2CH_2C_6H_5 + HCl + H_2O$$

Except for resinous products that were formed under certain conditions, bibenzyl was the only compound secured. No β-phenylethyl alcohol, $C_6H_5CH_2.CH_2OH$, was obtained; it was shown, however, that the reaction proceeded through intermediate formation of the aralkyl alcohol, for condensation of β-phenylethyl alcohol, benzene, and aluminum chloride in molecular equivalents at 100° gives 60.4 per cent of bibenzyl and a resinous substance.

Aliphatic Alcohols: Secondary

According to Huston and Hsieh [10] the reaction of 1 mole of isopropyl alcohol with 0.5 mole of aluminum chloride and 2 to 5 moles of benzene at below 30° gives isopropylbenzene in approximately 25 per cent yield. Norris and Sturgis [4] effected the reaction by using more than a molecular equivalent of aluminum chloride and heating the reaction mixture at 90-95° for six hours and then at 100° for six hours. They secured an appreciable quantity of ethylbenzene, together with isopropylbenzene and diisopropylbenzene. Tzukervanik and Tokareva [17] reacted 30 g of isopropyl alcohol, 150 cc of benzene, and 43 g of aluminum chloride, and secured 35 g of a fraction (b.p. 147-200°) consisting of isopropylbenzene and diisopropylbenzenes. When 100 cc of toluene was used instead of benzene, *p*-cymene was secured in 35-g yield.

[14] R. C. Huston and D. D. Sager, *J. Am. Chem. Soc.*, 48, 1955-1959 (1926).
[15] Swiss P. 166,491 (1934) to Soc. pour l'ind. chim. à Bâle, *C. A.*, 28, 5686; U. S. P. 1,970,353 (1934) to O. Albrecht (to Soc. pour l'ind. chim. à Bâle), *C. A.*, 28, 6822.
[16] S. Ishikawa and G. Maeda, *Sci. Rep. Tokyo Bunrika Daigaku*, A2, 157-164 (1937), *C. A.*, 31, 7860; *Brit. Chem. Abs.*-A (II), 405 (1937).
[17] I. Tzukervanik and K. Tokareva, *J. Gen. Chem. (U. S. S. R.)*, 5, 764-766 (1935), *C. A.*, 30, 442; *cf.* I. Tzukervanik, *J. Gen. Chem. (U. S. S. R.)*, 5, 117-120 (1935), *C. A.*, 29, 4768.

The condensation of *sec*-butyl alcohol with benzene and aluminum chloride gives a 70 per cent yield of *tert*-butylbenzene when 20 g of the alcohol, 100 cc of benzene, and 30 g of aluminum chloride are reacted.[17] It has been pointed out recently that although aluminum chloride catalyzes the condensation of *sec*-butyl alcohol with benzene to give a 69 per cent yield of *tert*-butylbenzene, the use of ferric chloride as the catalyst gives no reaction.[18] The use of 0.5 mole of aluminum chloride with 1 mole of the alcohol results in only a 25-28 per cent yield.[19]

When 20 g of *sec*-butyl alcohol are reacted with 100 cc of toluene in presence of 25 g of aluminum chloride, *p*-*sec*-butyltoluene, $CH_3.C_6H_4.CH(CH_3)(C_2H_5)$, is secured.[17]

Condensation of methyl-*n*-propyl carbinol and methylisopropyl carbinol with benzene in presence of an 0.5 molecular equivalent of aluminum chloride (with respect to the carbinol) at below 30° gave methyl-*n*-propylphenylmethane and methylisopropylphenylmethane, respectively, in 25-28 per cent yield.[19]

Aliphatic Alcohols: Tertiary

Norris and Sturgis [4] have found that if reaction of benzene with *tert*-butyl alcohol is effected by adding, during two hours, 0.6 mole of aluminum chloride to a mixture consisting of 0.5 mole of the alcohol and 3 moles of benzene kept at 0°, stirring the reaction mixture for two hours more at 0°, and then allowing it to come to room temperature and stand for 20 hours, an 84 per cent of theoretical yield of *tert*-butylbenzene is secured. The influence of temperature on this reaction is decided. If the same proportion of reactants are heated for six hours at 80°, and then for two hours at 95°, no *tert*-butylbenzene is formed. Instead, the reaction product consists of toluene, ethylbenzene, and isopropylbenzene.

The condensation of *tert*-butyl alcohol with *m*-xylene proceeds smoothly when reaction is effected by dropping, with vigorous stirring, a mixture of 1.75 moles of *m*-xylene and 0.3 mole of the alcohol into 0.9 mole of aluminum chloride held in a flask which is placed in a mixture of ice and salt. Upon stirring the mixture for five hours while still in the freezing bath, customary decomposition of the reaction product, and fractionation with a Fenske column, an 89 per cent yield of *sym*-*tert*-butylxylene (b.p. 205.5-206.5°) is secured. No butylated xylene was formed when 2 moles of catalyst were used with 1 mole of alcohol and the mixture was allowed to stand at room temperature for twelve hours. The product contains only toluene, isomeric xylenes, and tar.[20]

According to Potts and Dodson,[21] one mole of *tert*-butyl alcohol with 5 moles of benzene in presence of one mole of aluminum chloride gives a 50 per cent yield of *tert*-butylbenzene. Better yields were obtained when ferric chloride was used as catalyst, but ferric chloride does not effect condensation of primary and secondary alcohols with benzene.

[17] W. M. Potts and R. J. Dodson, *J. Am. Chem. Soc.*, 61, 2553 (1939).
[18] R. C. Huston and T. Y. Hsieh, *J. Am. Chem. Soc.*, 58, 439-441 (1936).
[19] J. F. Norris and B. M. Sturgis, *J. Am. Chem. Soc.*, 61, 1413-1417 (1939).
[21] W. M. Potts and R. J. Dodson, *J. Am. Chem. Soc.*, 61, 2553 (1939).

Tsukervanik [22] reports that benzene or toluene is easily alkylated with *tert*-butyl alcohol or with dimethylethyl carbinol in the presence of aluminum chloride. He reports 50-70 per cent yields of corresponding alkyl derivatives of benzene or toluene.

Huston and his co-workers [19,23] effected the condensation of *tert*-butyl-, *tert*-amyl-, the three *tert*-hexyl-, and the seven *tert*-heptyl alcohols with benzene by adding drop by drop, while vigorously stirring, 0.25 mole of the carbinol to a suspension of 0.5 mole of aluminum chloride in 1.25 moles of benzene at 20-30°, and allowing the reaction mixture to stand over night. The following products were secured with the indicated alcohols:

Carbinol	Product	Yield %
Trimethyl-	2-methyl-2-phenylpropane	65–70
Dimethylethyl-	2-methyl-2-phenylbutane	60
Dimethyl-*n*-propyl-	2-methyl-2-phenylpentane	55
Dimethylisopropyl-	2,3-dimethyl-2-phenylbutane	35
Methyldiethyl-	3-methyl-3-phenylpentane	40
Dimethyl-*n*-butyl-	2,4-dimethyl-2-phenylpentane	30
Dimethyl-*sec*-butyl-	2,3-dimethyl-2-phenylpentane	20
	2-chloro-2,3-dimethylpentane	10
Dimethyl-*tert*-butyl-	2,3,3-trimethyl-2-phenylbutane	7
Methylethyl-*n*-propyl-	2-ethyl-2-phenylbutane	40
	2-chloro-2-ethylpentane (2 g)	
Methylisopropyl-	2,3-dimethyl-2-phenylpentane	22
	3-chloro-2,3-dimethylpentane	14
Trimethyl-	3-ethyl-3-phenylpentane	40
	3-chloro-3-ethylpentane	2

The foregoing data indicate that the accumulation of alkyl groups on the carbon adjacent to the carbinol in *tert*-hexyl and heptyl alcohols has a depressing effect on the condensing ability of the compound, and that there is a tendency for *tert*-alkyl chlorides to form. Considerable amounts of unsaturated products were also obtained in reactions with these carbinols.

Aliphatic Alcohols with Naphthalene

Naphthalene has been found to be easily alkylated by primary, secondary, and *tert*-alcohols, generally forming mixtures of equal parts of mono- and dialkylnaphthalenes.[24] Here, as in analogous reactions with benzene, the amount of catalyst required varies with the nature of the alcohol. Whereas only 0.5 to 1 mole of aluminum chloride was found necessary with *tert*-alcohols, 1.5-2 moles were required with primary alcohols. The following condensations were effected from the indicated reactants in ligroin solution by digestion on a water-bath:

[22] I. Tsukervanik, *J. Gen. Chem. (U. S. S. R.)*, 5, 117-120 (1935); *C. A.*, 29, 4746.
[23] R. C. Huston, W. B Fox, and M. N. Binder, *J. Org. Chem.*, 3, 251-260 (1938). For condensation of dimethylamyl carbinols with benzene in presence of $AlCl_3$, see R. C. Huston, R. L. Guile, J J Soulati, and W. N. Wasson, *J. Org. Chem.*, 6, 253-9 (1941).
[24] I. P. Tsukervanik and I. Terent'eva, *J. Gen. Chem. U. S. S. R.*, 7, 637-640 (1937); *C. A.*, 31, 5780. A. E. Pavelkina, *J. Applied Chem. (U. S. S. R.)*, 12, 1423-1424 (1939); *C. A.*, 34, 3455.

Naphthalene	Alcohol	$AlCl_3$ (g)	Hours of heating	Product	% Yield
60 g	30 g $(CH_3)_2CHOH$	45	4	β-$C_{10}H_7CH\,.\,(CH_3)_2$ β,β-$C_{10}H_6[CH(CH_3)_2]_2$ $C_{10}H_6[CH(CH_3)_2]_3$	32.6 15.4 10.7
26 g	18.5 g $(CH_3)(C_2H_5)\,.\,CHOH$	37	5	α-$C_{10}H_7CH.(C_2H_5)(CH_3)$ $C_{10}H_6[CH(C_2H_5)(CH_3)]_2$	27.4 35.3
24 g	18.5 g $(CH_3)_3COH$	16.5	3	$C_{10}H_7\,.\,C(CH_3)_3$ $C_{10}H_6[C(CH_3)_3]_2$	21.5 37
24 g	20 g *tert*-amyl	17	2	$C_{10}H_6[C\,.\,(C_2H_5)\,.\,(CH_3)_2]_2$ β-$C_{10}H_7\,.\,C(C_2H_5)(CH_3)_2$	20 34

The condensation of oleyl alcohol with naphthalene in the presence of aluminum chloride has been claimed to give a product which may be converted to a synthetic detergent upon sulfonation.[25]

Aliphatic Alcohols with Chlorinated Aromatic Hydrocarbons

Condensation of alcohols with halogenated hydrocarbons in the presence of aluminum chloride proceeds analogously to that of unsubstituted aromatic hydrocarbons with formation of corresponding mono- and polyalkyl derivatives.[26] Reaction with primary alcohols proceeds most difficultly, a large excess of catalyst being required. With secondary alcohols, condensation is less difficult; tertiary alcohols react very easily. Excess aluminum chloride and higher temperatures are conducive to formation of polyalkyl derivatives. The following reactions were effected by gradual addition of aluminum chloride to a mixture of an aryl chloride and an alcohol and refluxing on a boiling water-bath for two to three hours:

Aryl Chloride	Alcohol	$AlCl_3$ (g)	Product
100 g Chlorobenzene	37 g *tert*-butyl	30	65% of isomeric *tert*-butylchlorobenzenes and 11 g of polyalkyl derivatives
100 g Chlorobenzene	44 g *tert*-amyl	25	50% of *p*- and *m*-*tert*-amylchlorobenzenes and 8 g of polyalkyl derivatives
100 g Chlorobenzene	60 g isopropyl	120	62% of chlorocumenes
100 g Chlorobenzene	44 g *sec*-butyl	50	50% of isomeric *sec*-butylchlorobenzenes and 8 g of polyalkyl derivatives
100 g Chlorobenzene	30 ml ethyl	120	40% of *p*-ethylchlorobenzene and 10 g of polyalkyl derivatives
150 g Chlorobenzene	74 g isobutyl	200	30% of monoalkyl- and 25 g of polyalkyl derivatives
100 g Chlorobenzene	44 g isoamyl	80	35% of monoalkyl and 15 g of polyalkyl-derivatives
25 g *o*-Chlorotoluene	19 g *tert*-butyl	15	45% of monoalkyl derivatives
120 g 1-Chloronaphthalene	44 g *tert*-amyl	30	60% of monoalkyl and 15 g of polyalkyl derivatives
75 g 1-Chloronaphthalene	80 g isopropyl	60	45% of isopropyl-1-chloronaphthalene and 12 g of polyalkyl derivatives

Aralkyl Alcohols

In 1916 Huston and Friedemann [27] reported that if benzene is mixed with benzyl alcohol and less than a molecular equivalent of aluminum

[25] Swiss P. 168,844 (1934) to Soc. pour l'ind. chim. à Bâle; *C. A.*, 29, 823.
[26] I. P. Tsukervanik, *J. Gen. Chem. (U. S. S. R.)*, 8, 1512-1515 (1938); *C. A.*, 33, 4587; *Brit. Chem. Abs.*-A (II), 282 (1939).
[27] R. C. Huston and T. E. Friedemann, *J. Am. Chem. Soc.*, 38, 2537-2533 (1916); *J. Chem. Soc. Abs.* (I), 19 (1917).

chloride is added, a vigorous reaction occurs with formation of diphenylmethane, *p*-dibenzylbenzene, *o*-dibenzylbenzene, anthracene, and a hydrocarbon, $C_{27}H_{24}$. By increasing the proportion of benzene used with respect to the benzyl alcohol, the yield of diphenylmethane was increased, and that of anthracene reduced. Later these investigators [28] found that an analogous reaction occurs with phenylmethyl carbinol and benzene in the presence of aluminum chloride at 25-30°. *asym*-Diphenylethane was secured in approximately 20 per cent yield, together with ethylbenzene, diphenylmethane, and anthracene. Varying conditions by decreasing the amount of catalyst and increasing the proportion of benzene gave a 65 per cent yield of diphenylethane. In the same way, phenylethyl carbinol gave 23-25 per cent of 1,1-diphenylpropane, 14 per cent of propylbenzene, 7 per cent of diphenylmethane, and about 5 per cent of anthracene. When reaction with benzhydrol was effected at below 10°, a 65-70 per cent yield of triphenylmethane was secured:

$$(C_6H_5)_2CHOH + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3CH + H_2O$$

Practically no diphenylmethane is formed, and the tarry residue is very small. Benzohydrol appears to condense more readily with benzene than does benzyl alcohol.

Although the foregoing secondary alcohols were found to undergo reaction at low temperatures in presence of less than a molecular equivalent of aluminum chloride, Huston and Hsieh [19] could not effect a condensation under like conditions when the primary aralkyl alcohols, phenylethyl and phenylpropyl alcohols, were used. More recently, however, it has been reported [29] that β-phenylethyl alcohol condenses with benzene at 100°, when 1 mole of the alcohol and 1 mole of aluminum chloride are used, with production of bibenzyl in 60.4 per cent yield:

$$C_6H_5 . CH_2 . CH_2 . OH + \qquad C_6H_5 . CH_2 . CH_2 . C_6H_5$$

Even under these more extreme conditions, however, condensation of α-phenylpropyl alcohol with benzene does not occur.

Cycloaliphatic Alcohols

The effect of strain in cycloalkyl carbinols on their reactivity with benzene in the presence of aluminum chloride is apparent in condensations effected with cyclohexyl-, cyclopentyl-, and cyclobutyl carbinols [30] Reaction was effected by treating a mixture of 1 mole of alcohol and 4 to 5 moles of benzene with two-thirds of a mole of aluminum chloride at low temperatures, 25-35°, or at high temperatures, 75-80°. The results are summarized:

[28] R. C. Huston and T. E. Friedemann, *J. Am. Chem. Soc.*, 40, 785-792 (1918); *J. Chem. Soc. Abs.*, 114, 209 (1918).
[29] S. Ishikawa and G. Maeda, *Science Reports Tokyo Bunrika Daigaku*, A3, 157-164 (1937); *C. A.* 31, 7260.
[30] R. C. Huston and K. Goodsmoot, *J. Am. Chem. Soc.*, 56, 2433-2434 (1934).

Product: -phenylmethane	% Yield, low temp	% Yield, high temp
Cyclohexyl-	0	7
Cyclopentyl-	0	45
Cyclobutyl-	29	21

Since strain is reduced to a minimum in the cyclohexyl group, it is the least reactive of the three carbinols investigated.

Reaction of cyclohexanol with benzene, however, is more readily effected if a greater proportion of aluminum chloride is used. Treatment of 25 g of the alcohol in 97.5 g of benzene with 33.4 g of aluminum chloride has been shown [29] to result in production of 18.5 g of phenylcyclohexane, 10 g of cyclohexene, and 0.5 g of 1,2-diphenylcyclohexane.

Condensation effected by using 40 g of cyclohexanol, 100 cc of benzene, and 35 g of aluminum chloride and heating on a water-bath for two hours, has been reported by Tsukervanik and Sidorowa [31] to result in a 62 per cent yield of cyclohexylbenzene and a 35 per cent yield of a mixture of di- and tricyclohexylbenzenes. Toluene was found to be less reactive, more catalyst and a large excess of the hydrocarbon being required. From 70 g of the alcohol, 80 g of the catalyst, and 200 cc of toluene, a 72 per cent yield of a fraction consisting of *p*- and *m*-cyclohexyltoluenes was secured. According to these investigators, the condensation probably proceeds through preliminary conversion of the alcohol into cyclohexene and cyclohexyl chloride, and subsequent reaction of the two products with the hydrocarbon:

$$C_6H_{11}OH \xrightarrow{AlCl_3} C_6H_{10} + AlCl_2OH + HCl$$

$$C_6H_{10} + HCl \xrightarrow{AlCl_3} C_6H_{11}Cl$$

$$C_6H_6 + C_6H_{10} \xrightarrow{AlCl_3} C_6H_6 . C_6H_{11}$$

$$C_6H_6 + C_6H_{11}Cl \xrightarrow{AlCl_3} C_6H_6 . C_6H_{11} + HCl$$

Later, these investigators [32] reported analogous reactions with substituted cyclohexanols. The following results were secured:

Hydrocarbon	Alcohol	Products	% Yield
Benzene	1,2-methylcyclohexanol	(methylcyclohexyl) benzene	42.5
Toluene	1,2-methylcyclohexanol	isomeric (methylcyclohexyl)-toluenes	50
Benzene	menthol	menthylbenzene	54.5
Toluene	menthol	*p*- and *m*-menthyltoluenes	61
Benzene	borneol	bornylbenzene	30
Toluene	borneol	*p*- and *m*-bornyltoluenes	64

[31] I. P. Tsukervanik and N. G. Sidorowa, *J. Gen. Chem. (U. S. S. R.)*, 7, 641-645 (1937); *C. A.*, 31, 5790.

[32] I. P. Tsukervanik and N. G. Sidorowa, *J. Gen. Chem. (U. S. S. R.)*, 8, 1899-1902 (1938); *C. A.*, 33, 5838.

It was found that in the preparation of menthylbenzene, the chief products were 3-menthene and menthyl chloride when insufficient aluminum chloride was used. In all the foregoing reactions, small amounts of polyalkylated hydrocarbons were obtained, but these were not identified

It has been observed [29] that the reaction of menthol with benzene, using 25 g of the alcohol, 62.5 g of benzene, and 21.5 g of aluminum chloride yields 41 g of 3-phenylmenthane, 30 g of *p*-3-menthene, and 7 g of high-boiling oxygenated compounds.

The condensation of a terpenic alcohol with benzene in the presence of aluminum chloride, followed by sulfonation of the resulting alkylated benzene, has been claimed to yield a wetting agent or synthetic detergent.[33]

Reaction of Alcohols with Phenols or Phenol Ethers

Condensation of alcohols with phenol ethers in the presence of aluminum chloride proceeds as the analogous reaction with aromatic hydrocarbons, with production of alkylated phenols or phenol ethers.

Primary and Secondary Aliphatic Alcohols

Huston and Hsieh [34] report that they were unable to effect condensation of ethyl, propyl, or butyl alcohol with phenol in the presence of aluminum chloride, and that in an attempted condensation with isopropyl alcohol, a compound was secured which did not correspond in properties to any of the known propylphenols or phenyl propyl ethers

According to Tsukervanik and Nazarova [35] the condensation of primary or secondary aliphatic alcohols with phenols or phenol ethers may be effected if an excess of catalyst and higher temperatures than those previously used are employed. Condensations with primary alcohols require 2 moles of catalyst to 1 mole each of phenol and alcohol. The following preparations are reported:

Phenol or ether	Alcohol	Reaction temp. (°C)	Hours of heating	Product	% Yield
Phenol	$(CH_3)_2CHOH$	110-120	6	*p*-$OH.C_6H_4.CH(CH_3)_2$	52
				nonphenolic fraction	23
Anisole	$(CH_3)_2CHOH$	120	4	*o*- and *p*-$CH_3O.C_6H_4.CH(CH_3)_2$	50
				o- and *p*-$OH.C_6H_4.CH(CH_3)_2$	38
Anisole	$(CH_3)_2CHOH$	130-140	4-6	*o*- and *p*-$CH_3O.C_6H_4.CH(CH_3)_2$	30
				o- and *p*-$OH.C_6H_4.CH(CH_3)_2$	64
m-Cresol	$(CH_3)_2CHOH$	125	6	$HO.C_6H_3(CH_3)CH(CH_3)_2$	68
				$(CH_3)_2CHO.C_6H_3(CH_3)CH(CH_3)_2$	20
Phenol	$(C_2H_5)(CH_3)CHOH$	130-140	6	$(C_2H_5)(CH_3)CH.C_6H_4.OH$	52
				$(C_2H_5)(CH_3)CHO.C_6H_4.CH(CH_3)(C_2H_5)$	13
Anisole	$(C_2H_5)(CH_3)CHOH$	100	2	$CH_3O.C_6H_4CH(CH_3)(C_2H_5)$	55
				$CH_3O.C_6H_3[CH(CH_3)(C_2H_5)]_2$	16
				$HO.C_6H_4.CH(CH_3)(C_2H_5)$	13

[33] U. S. P. 1,970,353 (1934) to O Albrecht (to Soc. pour l'ind. chim à Bâle; *C. A.*, **28**, 6332.
[34] R. C. Huston and T. Y. Hsieh, *J. Am. Chem. Soc.*, **53**, 439-441 (1930).
[35] I. P. Tsukervanik and Z. Nazarova, *J. Gen. Chem. (U. S. S. R.)*, **7**, 622-631 (1937), *C. A.*, **31**, 5778. I. P. Tsukervanik and Z. Nazarova, *Gen. Chem. (U. S. S. R.)*, **5**, 767-770 (1935), *C. A.*, **30**, 443 Z. M. Nazarova, *J. Gen. Chem. (U. S. S. R.)*, **8**, 1336-1340 (1938), *C. A.*, **33**, 4214.

Phenol or ether	Alcohol	Reaction temp. (°C)	Hours of heating	Product	Yield
Phenol	$(CH_3)(C_2H_7)CHOH$	20	24	phenolic fraction	57.5
		40-50	4	nonphenolic fraction	18
Anisole	$(CH_3)(C_2H_7)CHOH$	20	24	$CH_3O.C_6H_4.CH(C_2H_7(CH_3)$	
		40-50	4	$CH_3O.C_6H_3[CH(C_2H_7)(CH_3)]_2$	
Phenol	CH_3OH	no reaction			
Phenol	C_2H_5OH	120-140	6	diethylphenol	37.2
				o- and *p*-ethylphenol	24.5
				nonphenolic fraction	11
Phenol	propyl			*o*- and *p*-propylphenol	73.6
				$C_3H_7.C_6H_4.O.C_3H_7$	17
Phenol	butyl			phenolic products	72
				nonphenolic	14
Phenol	isobutyl			$(CH_3)_3C.C_6H_4.OH$ C_4H_9	
Phenol	isoamyl	160		3 amylphenols, one of which is $(CH_3)_2CH.CH(CH_3).C_6H_4.OH$	

As noted above, small amounts of dialkylphenol ethers, $R_2.C_6H_3.OR$, or alkylphenol ethers, $R.C_6H_4.OR$, are often formed during the reaction. Yield of the latter increases with decrease in the aluminum chloride concentration and temperature. The following series of reactions was advanced as possible steps in the process:

$$ROH + AlCl_3 \longrightarrow HCl + AlCl_2(OR)$$
$$C_6H_5OH + AlCl_3 \longrightarrow HCl + C_6H_5.O.AlCl_2$$
$$HCl + AlCl_2(OR) + C_6H_5.O.AlCl_2 \longrightarrow C_6H_5.OR + AlCl_3 + AlCl_2OH$$

The monoalkyl phenol ether is then converted to the ether of alkylphenol, $R.C_6H_4.OR$, by the action of excess catalyst or by higher temperatures. The conversion may be a saponification:

$$R.C_6H_4.OR + HCl \xrightarrow{AlCl_3} R.C_6H_4.OH + RCl$$

a rearrangement:

$$R.C_6H_4.OR + C_6H_5OH \xrightarrow{AlCl_3} 2R.C_6H_4.OH$$

or

$$2R.C_6H_4.OR \xrightarrow{AlCl_3} R.C_6H_4.OH + R_2.C_6H_3.OR$$

It has been reported [36] that *p-tert*-butylphenol is advantageously prepared if the alkylating agent is a mixture of butyl alcohols, butenes, and butyl chloride. The following yields were secured in various experiments by using the indicated reactants with phenol at 50-80°:

Expt.	Phenol (g)	*t*-butyl alcohol (g)	*t*-butyl chloride (g)	isobutyl chloride (g)	iso-butene (g)	$AlCl_3$ (g)	Yield
1	47	60	4	..	26.1	10	64.5
2	47	..	4	60	25.4	5	71.8
3	47	..	4	60	some	5	70.3
4	94	..	9	..	56	5	77.8

[36] V. I. Isagulyants and P. P. Bagryantseva, *Neftyanoe Khoz.*, 1938, No. 3, 36-41; *C. A.*, 33, 8153.

Experiment 3 was effected in carbon tetrachloride solution. Experiment 4 was carried out by using a temperature of 100° and a pressure of 5 atmospheres for two minutes.

Tertiary Aliphatic Alcohols

The condensation of phenol with tertiary aliphatic alcohols was effected by Huston and Hsieh [37] by treating an equimolecular mixture of phenol and alcohol suspended in petroleum ether with a half mole of aluminum chloride at 25-30°, and allowing the mixture to stand for several hours before decomposition with ice and hydrochloric acid. *p*-Alkylphenols in 45-60 per cent yields were secured from *tert*-butyl, *tert*-amyl, and the three *tert*-hexyl alcohols. Tzukervanik and Nazarova [38] report that condensation of *tert*-butyl alcohol or of dimethylethyl carbinol with phenol and aluminum chloride proceeds analogously to that with benzene and toluene, giving 60-70 per cent yields of alkyl phenols. Considerable amounts of olefins and alkyl halides were also produced.

Using a half mole of aluminum chloride with a molecular equivalent of alcohol, condensations of phenol with the following *tert*-heptyl alcohols were also effected, with formation of the indicated *p*-hydroxyphenylmethanes from the corresponding carbinols [39]:

Product: *p*-hydroxyphenylmethane	% Yield	m p (°C)
n-butyldimethyl-	64.6	16–17
isobutyldimethyl-	44.4	31–32
sym-butyldimethyl-	27.3	49–50.5
tert-butyldimethyl-	25.8	133–134
n-propylmethylethyl-	30.7	.....
isopropylmethylethyl-	40.6	42–43
triethyl-	30.0	75.5–76.5

Reaction of *tert*-dimethylamyl carbinols with phenols has been effected by dissolving 32 g of the alcohol and 28 g of phenol in 100 cc of petroleum ether and adding dropwise during two hours 17 g of aluminum chloride suspended in 150 cc of petroleum ether at 25-30°, and allowing the mixture to stand over night. The following products were secured in the indicated yields from the corresponding *tert*-octyl alcohol and phenol [40]:

	% Yield
2-methyl-2-*p*-hydroxyphenylheptane	69.5
2,3-dimethyl-2-*p*-hydroxyphenylhexane	35.5
2,4-dimethyl-2-*p*-hydroxyphenylhexane	58.5
2,5-dimethyl-2-*p*-hydroxyphenylhexane	64.6
2-methyl-3-ethyl-2-*p*-hydroxyphenylpentane	28.3
2,4,4-trimethyl-2-*p*-hydroxyphenylpentane	64.6
2,3,4-trimethyl-2-*p*-hydroxyphenylpentane	23.1
2,3,3-trimethyl-2-*p*-hydroxyphenylpentane	2.1

[37] R. C. Huston and T. Y. Hsieh, *J. Am. Chem. Soc.*, **58**, 439-441 (1936)
[38] I. Tzukervanik and Z. Nazarova, *J. Gen. Chem. (U. S. S. R.)*, **5**, 767-770 (1935); *C. A.*, **30**, 411
[39] R. C. Huston and G. W. Hedrick, *J. Am. Chem. Soc.*, **59**, 2001-2003 (1937).
[40] R. C. Huston and R. L. Guile, *J. Am. Chem. Soc.*, **61**, 69-70 (1939).

The manufacture of alkylphenols by condensation of a monohydric *tert*-aliphatic alcohol with a phenol at 0-50° in the presence of aluminum chloride and preferably a diluent, such as light petroleum, has been patented.[41]

Aralkyl Alcohols

Benzylation of phenol, effected by treating a suspension of 1 molecular equivalent of benzoyl alcohol and 1.1 equivalents of phenol in petroleum ether with 0.5 molecular equivalent of aluminum chloride at 20-30°, gives a 43-45 per cent yield of *p*-benzylphenol[42]:

$$C_6H_5.CH_2OH + C_6H_5.OH \longrightarrow C_6H_5.CH_2.C_6H_4OH + H_2O$$

The yield was not increased by using a molecular equivalent of catalyst. When the reaction was effected in absence of solvent, poorer results were secured.

Substitution of anisole for phenol, according to the method described above for production of *p*-benzylphenol, gives a 46 per cent yield of the methyl ether of *p*-benzylphenol; with phenetole, a 57 per cent yield of the ethyl ether of *p*-benzylphenol was analogously secured.[42]

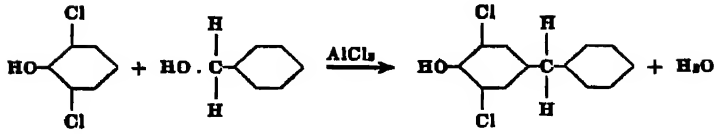
Benzylation of *o*-cresol, effected by treatment of a mixture of 100 g of the phenol and 100 g of benzyl alcohol in 200 g of petroleum ether with 65 g of aluminum chloride at 30-35° gives 2-methyl-4-benzylphenol as main product, together with small amounts of 2-methyl-6-benzylphenol and 2-methyl-4,6-dibenzylphenol.[43]

Reaction of *m*-cresol with benzyl alcohol effected by gradual addition of 60 g of aluminum chloride over a period of two hours to a mixture consisting of 120 g of *m*-cresol, 100 g of benzyl alcohol in 150 g of petroleum ether at 35° results in formation of two monobenzyl cresols, 3-methyl-4-benzylphenol and 3-methyl-6-benzylphenol, together with one dibenzyl cresol, 3-methyl-4,6-dibenzylphenol.[44]

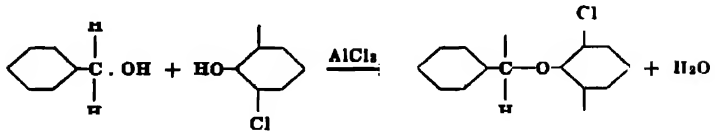
Condensation of *p*-cresol with benzyl alcohol in the molecular ratio of 2:1 by treatment with 0.5 mole of aluminum chloride in petroleum ether solution at below 30° gives a 35 per cent yield of crude 2-benzyl-4-methylphenol and a 36 per cent yield of 2,6-dibenzyl-4-methylphenol. When a 3:1 ratio of reactants was employed, with the same amount of aluminum chloride, a 53 per cent yield of the monobenzyl compound and 30 per cent yield of the dibenzyl compound resulted.[45]

In the reaction of benzyl alcohol with 2,6-dichlorophenol in presence of aluminum chloride, Huston and Eldridge[46] secured not only the expected 3,5-dichloro-4-hydroxydiphenylmethane,

[41] U. S. P. 2,051,800 (1936) to R. C. Huston (to Michigan State Board of Agriculture); *Brit. Chem. Abs.*-B, 1023 (1937).
[42] R. C. Huston, *J. Am. Chem. Soc.*, 46, 2775-2779 (1924).
[43] R. C. Huston, H. A. Swartout, and G. K. Wardwell, *J. Am. Chem. Soc.*, 52, 4484-4489 (1930).
[44] R. C. Huston and A. V. Houk, *J. Am. Chem. Soc.*, 54, 1506-1510 (1932).
[45] R. C. Huston and W. C. Lewis, *J. Am. Chem. Soc.*, 53, 2379-2383 (1931).
[46] R. C. Huston and E. F. Eldridge, *J. Am. Chem. Soc.*, 53, 2260-2264 (1931).



but also 2,6-dichlorophenylbenzyl ether,



The condensation of 1 mole of methylphenyl carbinol, ethylphenyl carbinol, or benzhydrol with one mole of phenol in presence of 0.5 mole aluminum chloride proceeds with formation of the expected hydroxy di- or tri-aryl paraffins.[47] Methylphenyl carbinol gives a 33-35 per cent yield of *p*-hydroxy-1,1-diphenylethane:

$$C_6H_5.CH(OH)(CH_3) + C_6H_5.OH \qquad C_6H_5.C(CH_3)H.C_6H_4.OH + H_2O$$

A 27-30 per cent yield of *p*-hydroxy-1,1-diphenylpropane is secured from ethylphenyl carbinol:

$$C_6H_5.CH(OH)(C_2H_5) + C_6H_5.OH \qquad C_6H_5.C(C_2H_5)H.C_6H_4.OH + H_2O$$

From benzhydrol a 40 per cent yield of *p*-hydroxytriphenylmethane is obtained:

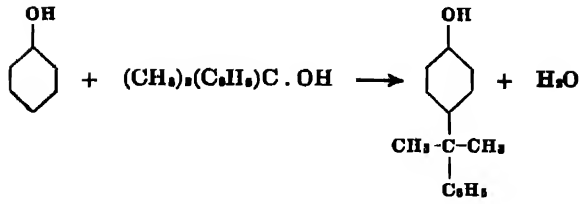
$$(C_6H_5)_2CHOH + C_6H_5.OH \qquad (C_6H_5)_2CH.C_6H_4.OH + H_2O$$

The fact that the best yield is obtained with benzhydrol, in which both alpha carbons are members of the unsaturated ring, has been pointed out as additional evidence of the accelerating effect of the unsaturation of the alpha-carbon on the reactivity of the alcoholic hydroxy- group

Using the same proportion of reactants, phenylpropyl carbinol gave only a 20 per cent yield of 4-(α-phenylbutyl)phenol and a 6 per cent yield of 2-(α-phenylbutyl)phenol.[48]

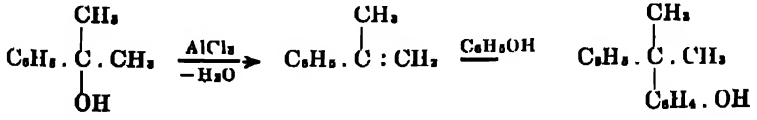
The reaction of tertiary aryl-substituted carbinols with phenol in the presence of aluminum chloride has been recently investigated by Welsh and Drake.[49] The condensation of dimethylphenyl carbinol was effected by adding rapidly, with stirring, 0.083 mole of aluminum chloride to 0.53 mole of molten phenol, heating the mixture on a steam-bath while 0.167 mole of the carbinol with 16 g of phenol were added dropwise, and then heating and stirring the reaction mixture for one hour. A 72 per cent yield of *p*-(α,α-dimethylbenzyl)phenol was secured:

[47] R. C. Huston, W. C. Lewis, and W. H. Grotemut, *J. Am. Chem. Soc.*, 49, 1365-1368 (1927).
[48] R. C. Huston and H. W. Strickler, *J. Am. Chem. Soc.*, 55, 4317-4318 (1933).
[49] L. W. Welsh and N. L. Drake, *J. Am. Chem. Soc.*, 60, 89-92 (1938).



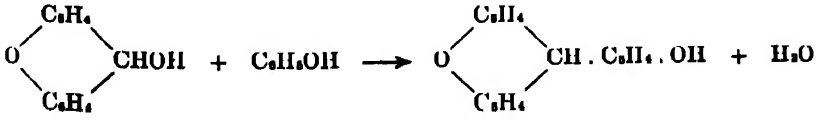
It was found that the yield of alkylated phenol was adversely affected by temperatures below 100° and aluminum chloride in excess of 0.5 mole per mole of carbinol because of increased formation of hydrindene derivatives. Using molar proportions of phenol and carbinol with 0.5 mole of catalyst at 20-30°, yield of the alkylated phenol was only 30-40 per cent.

Condensation of phenol with methyldiphenyl carbinol or triphenyl carbinol was carried out under the optimum conditions given above for the mono-aryl carbinol. Reaction proceeded more readily as the aryl content of the carbinol was increased. Thus, an 80 per cent yield of *p*-(α,α-diphenylethyl)phenol was secured from methyldiphenyl carbinol, and a 95 per cent yield of triphenylmethylphenol from triphenyl carbinol. Resinous materials were formed as by-products in the reactions with mono- and di-aryl carbinols. Their formation may be assumed to indicate formation of olefins and a reaction mechanism involving the addition of phenol at the double bonds of the olefin:



Such a mechanism is also indicated by the production of *sym*-tetraphenylethane, instead of the unsymmetrical isomer, in the condensation of benzyldiphenyl carbinol with benzene in the presence of aluminum chloride.[50]

Condensation of xanthydrol and phenol, with formation of 4-hydroxyphenylxanthane, may be effected in presence of aluminum chloride:



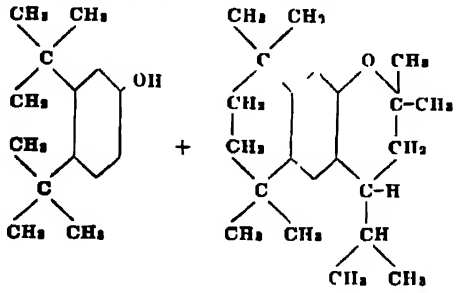
Analogous reactions have been shown to occur when phenol is replaced by *p*-chlorophenol, α-naphthol, *p-tert*-(2′-phenyl)butyl phenol, and *p-tert*-(2′-phenyl)amyl phenol. Reaction is effected by refluxing for eight hours a benzene solution of the reactants.[51]

[50] L. H. Welsh, Master's thesis, University of Maryland, 1935.
[51] J. B. Niederl and W. F. Hart, *J. Am. Chem. Soc.*, 59, 719-720 (1937).

Ditertiary-1,4-Glycols

The formation of higher ring compounds by reaction of ditertiary-1,4-glycols with aromatic hydrocarbons, phenols, or phenol ethers occurs in the presence of aluminum chloride.[52] 2,5-Dimethylhexane-2,5-diol and phenol yield 5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-2-naphthol and a smaller quantity of a chromane derivative, produced by further reaction of the substituted naphthol with another mole of the alkylating agent

$$(CH_3)_2C(OH)CH_2CH_2(OH)C(CH_3)_2 \xrightarrow{C_6H_5OH + AlCl_3}$$



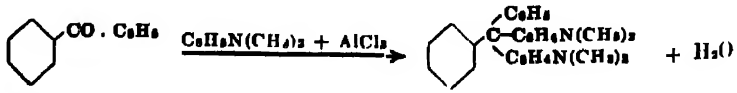
The condensation probably occurs through primary formation of a monoalkyl derivative of phenol which immediately undergoes cyclization by elimination of water; however, the intermediate product could not be isolated.

1,1,4,4-Tetraphenylbutane-1,4-diol was shown to undergo a similar reaction with *o*-cresol.

The reaction, involving both alkylation and cyclization, has been termed cycli-alkylation. Similar condensation products are obtained by using ditertiary 1,4-dichlorides, 1,5-diolefins, and 2,2,5,5-tetraalkyltetrahydrofurans instead of the 1,4-glycols.

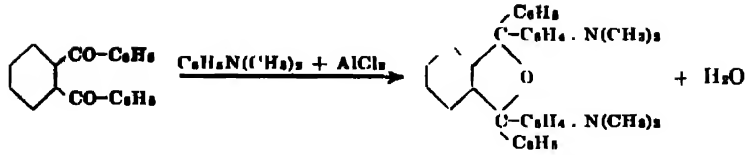
Replacement of Oxygen from Ketonic and Carboxy Groups

In 1907, Haller and Guyot [53] reported that *tert*-aromatic amines condensed with compounds containing the carbonyl group, in presence of aluminum chloride, to give substitution products in which the keto-oxygen had been replaced by the amine, substitution occurring *p*- to the amino group. Condensation occurred with cleavage of water. Benzophenone and dimethylaniline yielded bis-(*p*-dimethylaminophenyl)diphenylmethane



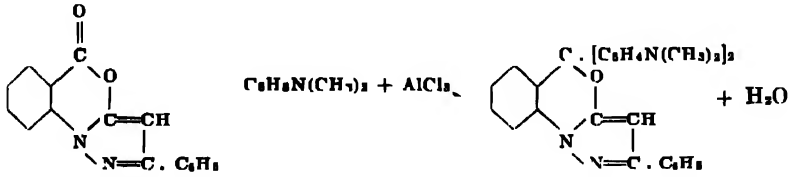
o-Bibenzoyl reacts with dimethylaniline probably according to the scheme:

[52] H. A. Bruson and J. W. Kroger, *J. Am. Chem. Soc.*, 62, 38-44 (1940).
[53] A. Haller and A. Guyot, *Compt. rend.*, 144, 847-851 (1907); *C. A.*, 1, 2290.



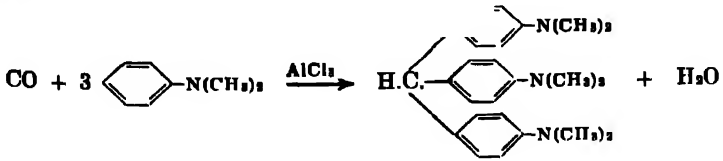
Similar reactions were found to occur with dimethylaniline and benzil, isatin, indigotin, ethyl phenylglyoxylate, ethyl oxalate, and anthraquinone.

An analogous condensation occurs when 3-phenylpyrazoisocumarazone is reacted with dimethylaniline [54]:



In studying the condensation of aromatic monoketones with tertiary aromatic amines under the influence of aluminum chloride, Courtot and Ouperoff [55] found that benzophenone is converted by dimethylaniline and aluminum chloride at 40-50° into *p*-dimethylaminotriphenyl carbinol, but that at 75-85°, *p*-dimethylaminotriphenylmethane is produced. Under all conditions of temperature, malachite green is obtained only in minute amount. Condensation does not take place with Michler's ketone, but phenyl α- or β-naphthyl ketone and fluorenone react with dimethylaniline as does benzophenone. The reaction with fluorenone is so exothermic that the ether used as solvent is caused to boil.

Carbon monoxide reacts with dimethylaniline in the presence of aluminum chloride and under superatmospheric pressure to give up to 70 per cent yields of leuco crystal violet based on unrecovered dimethylaniline.[56] The total reaction is,



but it has been assumed to proceed through intermediate formation of *p*-dimethylaminobenzaldehyde, which then condenses with 2 moles of dimethylaniline to give the final product:

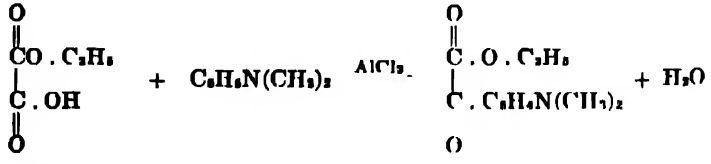
$$(CH_3)_2N\,.\,C_6H_4\,.\,CHO + 2C_6H_5N\,.\,(CH_3)_2 \longrightarrow [(CH_3)_2N\,.\,C_6H_4]_2CH + H_2O$$

[54] A. Michaelis, *Ann.*, 373, 129-213 (1910); *C. A.*, 4, 2138.
[55] C. Courtot and V. Ouperoff, *Compt. rend.*, 191, 214-216 (1930); *Brit. Chem. Abs.*-A, 1184 (1930).
[56] T. R. Liston and W. M. Dehn, *Ind. Eng. Chem.*, 26, 1073-1074 (1934).

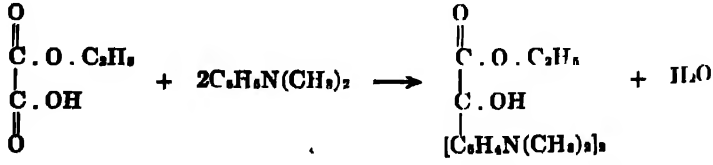
In an attempt to apply this reaction to aralkyl, aliphatic, and hydroaromatic ketones, it was found [57] that in most cases self-condensation of the ketone occurs when it is treated with dimethylaniline and aluminum chloride. The following results were secured with the indicated ketones:

Ketone	Product
Acetophenone	50% of triphenylbenzene
Styryl methyl ketone	non-basic resins
Phenyl styryl ketone	a double compound (at 30-40°) which undergoes fission at 91-92° to give leuco-malachite green
α-Indanone	anhydro-bis-indanone and truxene
Acetone	mostly amino reaction product but also the ketol, $C_8H_{16}O_2$
Diethyl ketone	dipropione alcohol
Cyclohexanone	at 40-50° gives 1,1-tetramethyldiaminodiphenylcyclohexane; at 10-20°, cyclohexylene-2-cyclohexanone is formed exclusively
Cyclopentanone	at 15° no isolable product; at 10° yields anhydro-bis-cyclopentanone
Cycloheptanone	cycloheptylenecycloheptanone
Camphor	unaffected

The condensation of oxalic esters with *tert*-aromatic amines has been extensively studied by Guyot.[58] When a solution of ethyl oxalate and dimethylaniline in anhydrous ether is added to a solution of aluminum chloride in dry ether, a 60 per cent of theoretical yield of ethyl (*p*-dimethylaminophenyl)glyoxylate is secured:



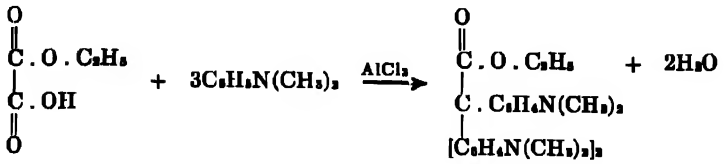
In the presence of an excess of dimethyl aniline, but not an excess of aluminum chloride, the product consists almost entirely of ethyl bis(*p*-dimethylaminophenyl)glycolate:



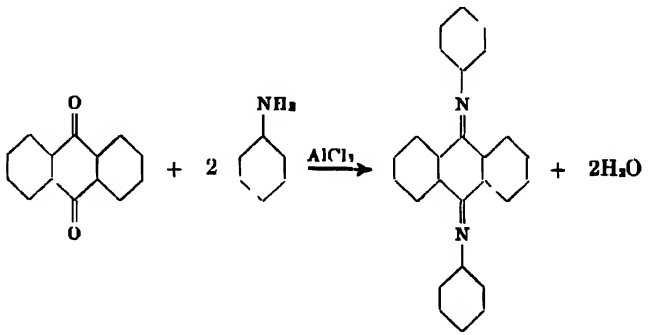
At higher temperatures and in the presence of an excess of aluminum chloride and of dimethylaniline, reaction occurs with both the carbonyl

[57] C. Courtot and V. Ouperoff, *Compt. rend.*, 191, 416-418 (1930); *Brit. Chem. Abs.-A*, 1291 (1930)
[58] A. Guyot, *Compt. rend.*, 144, 1031-1033, 1120-1122 (1907); *J. Chem. Soc. Abs.*, 92 (I), 640 (1907)

and the hydroxy groups. Ethyl tris(dimethylaminophenyl)acetate is secured:



When compounds containing a carbonyl group are condensed with primary or secondary aromatic amines, reaction occurs with displacement of N-hydrogen. Aniline and anthraquinone yield anthraquinone-9,10-dianil [59]:

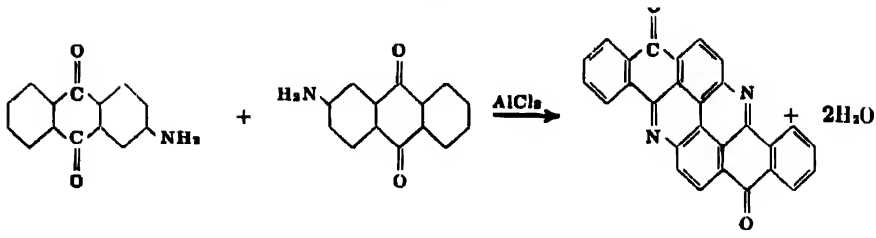


It has been claimed [60] that when ketoanils, or their primary constituents, are heated with aluminum chloride, decomposition occurs with formation of derivatives of 2-methylquinoline in over 90 per cent yield, and a paraffinic hydrocarbon. Conversions reported include:

Initial Constituent	Products
Acetone anil (or acetone, aniline, and aniline-HCl)	2,4-dimethylquinoline and methane
Ethylmethylketo anil (or aniline, aniline HCl, and methylethyl ketone)	2-methyl-4-ethylquinoline and ethane
Acetone, *p*-toluidine, and p-toluidine hydrochloride	2,4,6-trimethylquinoline and methane
Acetophenone anil	4-phenyl-2-methylquinole, aniline, and benzene

The autocondensation of 2-aminoanthraquinone to flavanthrene is effected by treating the quinone in presence of aluminum chloride.[61]

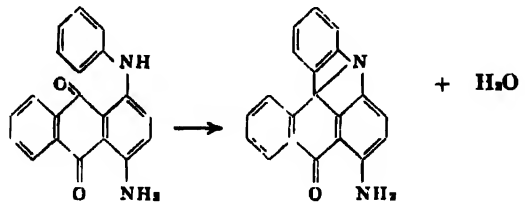
[59] German P. 520,484 to I. G.
[60] German P. 362,583 and 363,583 (1922) to Knoll & Co.; *J. Chem. Soc. Abs.*, 124 (I), 946 (1923); *C. Z.*, 1923 II, 915.
[61] R. Scholl, *Ber.*, 40, 1691-1702 (1907), *J. Chem. Soc Abs.*, 92 (I), 540 (1907); German P. 188,119 to R. Scholl; *cf.* U. S. P. 900,800 (1909) to M. H. Isler to Badische Anilin und Soda Fabrik; U. S. P. 793,145 (1905) to R. Bohn to Badische Anilin und Soda Fabrik.



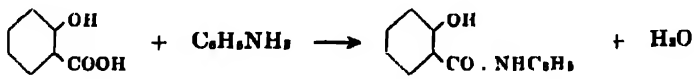
Here there is not only condensation of the amino group with the carbonyl, but also a dehydrogenation.

Fusion of 2,2′-diphthalimidobiphenyl (from 2,2′-diaminobiphenyl and phthalic anhydride) with aluminum chloride and sodium chloride at 160-250° for ten hours yelds flavanthrene.[62]

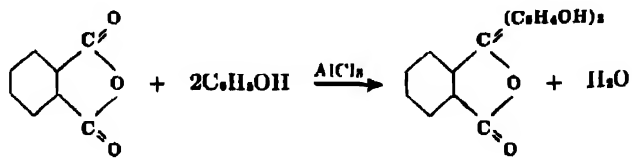
An interesting intramolecular condensation is that of 1-anilino-4-aminoanthraquinone to yield 4-aminocoeramidonin [63]:



Aluminum chloride has been claimed to be an effective catalyst for the condensation of a carboxylic acid with an amine. Thus salicylic acid and aniline readily react to yield salicyl anilide [64]



Under certain conditions, phenols replace a keto-oxygen of phthalic anhydrides. With phenol, phenolphthalein is secured:



However, the preparation of phenolphthalein is better effected in presence of zinc chloride, a milder catalyst.[65] Aluminum chloride is gener-

[62] V. Krepelka and R. Stefec, *Collection Czechoslov. Chem. Communs.*, 9, 29-34 (1937); *C. A.*, 31, 3909.

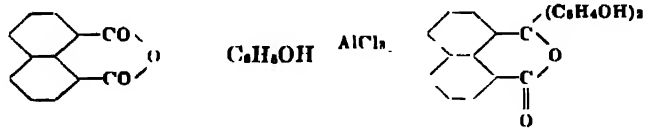
[63] French P. 696,868 to I. G. Farbenind.

[64] U. S. P. 1,972,142 to R. Goldstein (to Imperial Chem. Industries); *C. A.*, 28, 6445 (1934).

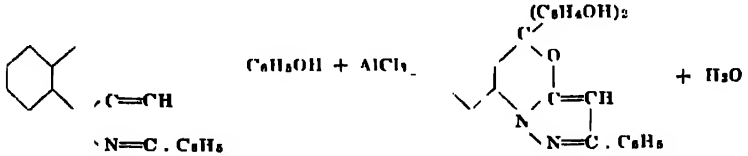
[65] *C. F. Ward, J. Chem. Soc.*, 119, 850-852 (1921); *C. A.*, 15, 2862. See U. S. P. 2,193,485 (1940) to M. Hubacher (to Exlax, Inc.) for the use of a mixture of aluminum chloride with zinc chloride as catalyst for this reaction.

ally used for effecting the addition of phenols to phthalic anhydride with formation of hydroxy keto-acids.* In this case, at least two moles of the catalyst to one mole of phthalic anhydride are required. The use of molecular equivalents of phthalic anhydride and aluminum chloride results in the formation of phthaleins.

Naphthalic anhydride and phenol readily yield phenolnaphthalein in the presence of aluminum chloride; whereas with zinc chloride, tin tetrachloride, or sulfuric acid, the condensation does not take place.[66]

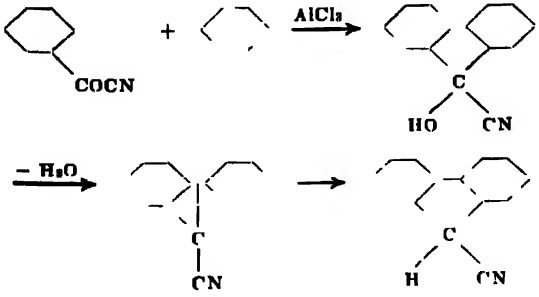


3-Phenylpyrazoisocumarazone condenses with phenols; reaction occurs with replacement of the keto-oxygen [67]:



The condensation of benzoyl cyanide with aromatic hydrocarbons or phenol ethers has been investigated by Vorländer.[68] 9-Cyanofluorene and a little benzil are formed if reaction is conducted at room temperature and in the presence of aluminum chloride and hydrogen chloride. Triphenylacetonitrile is secured when heating is employed during condensation, and no hydrogen chloride is used as catalyst.

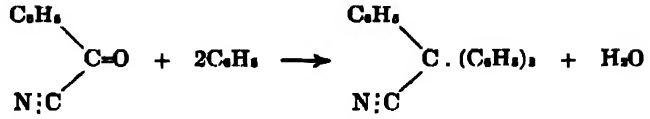
In the cold:



* See page 530.

[66] G. F. Jaubert, *Ber.*, **28**, 991-994 (1895).
[67] A. Michaelis, *Ann.*, **373**, 129-212 (1910); *C. A.*, **4**, 2138.
[68] D. Vorländer, *Ber.*, **44**, 2455-2476 (1911); *C. A.*, **5**, 3817.

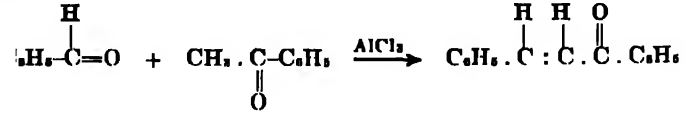
Reaction with heating:



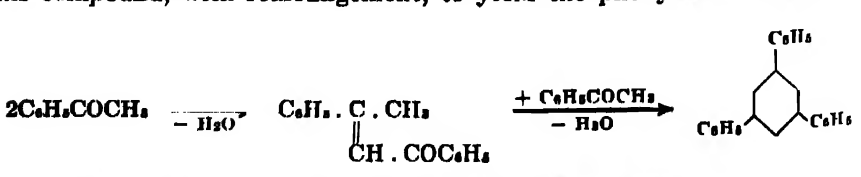
The condensation of benzoyl cyanide with toluene, ethyl benzene, anisole, or phenetole proceeds with formation of triarylacetonitriles in good yields. Thus 7 g of benzoyl cyanide, 13 g of anisole in the presence of 20 g of aluminum chloride in carbon disulfide at 0-10° gave 15 g of bis(4-methoxyphenyl)phenylacetonitrile, m.p. 98°. The reaction was also shown to be applicable to derivatives of benzoyl cyanide.

In investigating optimum conditions for Friedel-Crafts ketone synthesis, Calloway and Green [69] noted that evolution of hydrogen chloride continues as long as the reaction mixture is refluxed. Investigation of a residue resulting from the synthesis of acetophenone revealed the presence of dypnone. That this was produced by the autocondensation of acetophenone was shown by the fact that reaction of two moles of acetophenone in presence of one mole of aluminum chloride gave a 73 per cent yield of dypnone:

When benzaldehyde was substituted for one mole of acetophenone condensation in the presence of aluminum chloride gave a 91 per cent yield of chalcone:

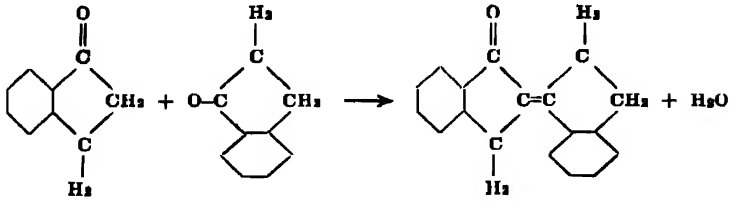


In attempting the reaction of various aliphatic, alicyclic, and arylalkyl ketones and dimethylaniline with aluminum chloride, the self-condensation of acetophenone, acetone, cyclohexanone, cyclopentanone, and cycloheptanone was noticed in varying degrees.[70] Acetophenone was converted to 1,3,5-triphenylbenzene in 50 per cent yield. The formation of this compound probably involves primary formation of 7-methylbenzalacetophenone and subsequent addition of more acetophenone to this compound, with rearrangement, to yield the phenylated benzene [71]:



[69] N. O. Calloway and L. D. Green, *J. Am. Chem. Soc.*, **59**, 809-811 (1937).
[70] C. Courtot and V. Ouperoff, *Compt. rend.*, **191**, 416-418 (1930), *C. A.*, **24**, 5719.
[71] *cf.* C. Engler and L. Dengler, *Ber.*, **26**, 1444-1449 (1893).

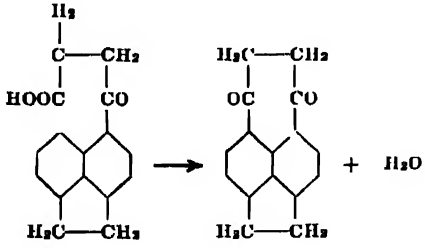
Indanone undergoes autocondensation in the presence of aluminum chloride to yield anhydro-bis-indanone [70]:



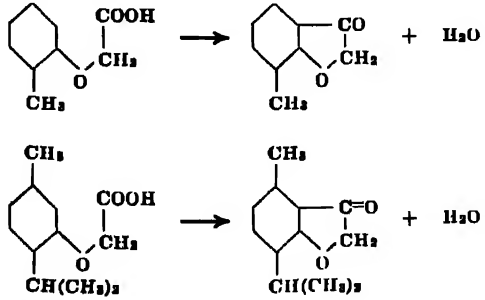
Ring Closure of Carboxylic Acids

Intramolecular ring closure of keto-carboxylic acids, when effected with aluminum chloride, is generally conducted by preliminary conversion to the acid chloride.* Under stringent conditions, however, ring closure of the acid itself occurs.

Upon heating β-(3-acenaphthoyl)propionic acid in molten sodium aluminum chloride, ring closure occurs with formation of a seven-membered ring [72]:



o-Tolyloxyacetic acid and 3-methyl-6-isopropylphenoxyacetic acid undergo ring closure when treated with aluminum chloride, with formation of corresponding coumaran-3-ones [73]:

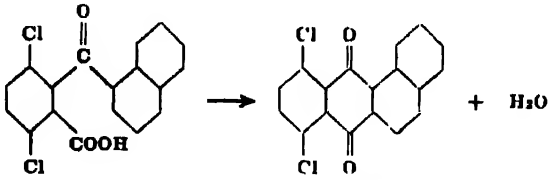


* See Chapter 7.

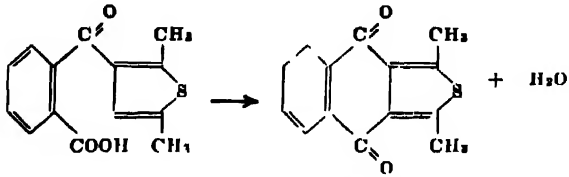
[70] L. F. and M. A. Peters, *J. Am. Chem. Soc.*, 54, 4347-4356 (1932).

[72] E. Mameli, *Gazzetta*, 52, 322-337 (1922); *J. Chem. Soc. Abs.*, 122 (I), 669 (1922).

Although ring closure of aroylbenzoic acids is generally effected with sulfuric acid, aluminum chloride has been used in some cases.[74] 2-α-Naphthoyl-3,6-dichlorobenzoic acid thus yields 5,8-dichloro-1,2-benzanthraquinone:



Heating (2,5-dimethyl-3-thenoyl)-*o*-benzoic acid in an $AlCl_3$-NaCl melt at 140° for five minutes converts it into 2,7-dimethyl-β-thiophanthrenequinone in an 18 per cent of theoretical yield [75]:



The use of an $AlCl_3$-NaCl melt for effecting intramolecular ring closure of dithionaphthenyl ketonic acids, with formation of dithionaphthenyl quinones, is described by Mayer,[76] who applied the reaction to the preparation of dyestuffs of the thianaphthene series.[77]

The cyclization of keto-acids with aluminum chloride is important only in cases where sulfuric acid causes sulfonation before ring closure, as in the case of phenylbenzoylbenzoic acid. Here the original Friedel-Crafts aluminum chloride complex of the keto-acids can be heated directly with nitrobenzene to give the corresponding phenylanthraquinone. Practically all aluminum chloride complexes of keto-acids, when treated similarly, yield anthraquinone derivatives.[78]

Reaction of Saturated Aldehydes with Aromatic Compounds

Aliphatic Aldehydes

Since the condensation of halogenated aliphatic aldehydes with aromatic hydrocarbons in the presence of aluminum chloride has been reported by early investigators to proceed with replacement of halogen, reactions effected with halogenated aldehydes are discussed in the sections of this book dealing with Friedel-Crafts alkylations.* Frankforter and his co-workers [79] have concluded, however, that the condensation of

[74] *cf.* German P. 529,970 to I. G.; Brit P. 332,192 (1930) to M. A. Kuns and K. Koberle (to I G.); *C. Z.*, 1931 I, 3400.
[75] W. Steinkopf, T. Barlag, and H. J. v. Petersdorff, *Ann.*, 540, 7-14 (1939).
[76] F. Mayer, *Ann.*, 488, 259-298 (1931).
[77] *cf.* Brit. P. 266,498 (1928) to I. G.; *Brit. Chem. Abs.*-B, 45 (1930).
[78] P. H. Groggins, *Personal communication.*
* See page 144.
[79] G. B. Frankforter and W. Kritchevsky, *J. Am. Chem. Soc.*, 36, 1511-1520 (1914); *ibid.*, 37, 385-392 (1915). E. E. Harris and G. B. Frankforter, *ibid.*, 48, 3144-3150 (1926).

chloral or bromal with aromatic hydrocarbons or phenol ethers in presence of aluminum chloride proceeds as the Baeyer reaction, with elimination of water and production of halogenated aromatic hydrocarbons.

In order to study more thoroughly the reactions of chloral, chloral hydrate, and bromal with certain organic compounds in the presence of aluminum chloride, a series of studies on the action of trioxymethylene with aromatic hydrocarbons and aluminum chloride was undertaken. The trioxymethylene used was evidently paraformaldehyde, which according to the investigations of Staudinger,[80] is a mixture of polyoxymethylene glycols, $HO.CH_2O.(CH_2O)_xCH_2OH$ with x = less than 100.

Frankforter and Kokatnur [81] reported that trioxymethylene generally reacted with aromatic hydrocarbons, as did the halogenated aldehydes mentioned above. The variations observed seemed to be influenced only by physical factors, such as the temperature used and the manner in which the aluminum chloride was added. These workers mistakenly assumed that trioxymethylene had a ring structure which would be broken during the condensation, thus permitting reaction with terminal groups of the resulting chain. They referred to earlier work of Grassi-Cristaldi and Maselli,[82] in which the ring had presumably been broken by hydrochloric acid to give formaldehyde and a hydrochloride, $ClCH_2OH$. Grassi-Cristaldi and Maselli had reported the production of diphenylmethane by first treating paraformaldehyde with hydrogen chloride and subsequent reaction of this product with benzene and aluminum chloride. Later, however, Litterscheid [83] showed that the production of diphenyl methane proceeded not through the intermediate formation of chloromethyl alcohol, but through dichlorodimethyl ether (formed from hydrogen chloride and formaldehyde), which subsequently reacted with 2 moles of benzene to give benzyl chloride.

Frankforter and Kokatnur also obtained diphenylmethane, together with an equal amount of anthracene, by treating their trioxymethylene with benzene and aluminum chloride. They assumed that the following reaction occurs:

$$4C_6H_6 + (CH_2O)_3 + AlCl_3 \longrightarrow CH_2(C_6H_5)_2 + C_{14}H_{10} + 3H_2O + AlCl_3 + H_2$$

With toluene they secured ditolylmethane and dimethylanthracene, and assumed that the course of the reaction was the same as that with benzene. Using *p*-xylene, they report the formation of dixylylmethane and the formation of dimesitylmethane with mesitylene.

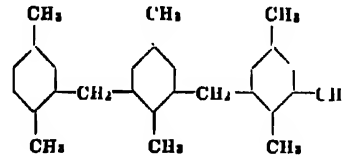
Subsequently, Huston and Ewing [84] showed that the reaction of *p*-xylene with trioxymethylene does not give predominantly dixylylmethane and tetramethylanthracene, as had been assumed by Frank-

[80] H. Staudinger, *Ann.*, 474, 241 (1929).
[81] G. B. Frankforter and V. R. Kokatnur, *J. Am. Chem. Soc.*, 36, 1529-1537 (1914).
[82] G. Grassi-Cristaldi and C. Maselli, *Gass.*, 28 (II), 477-500 (1898); *J. Chem. Soc. Abs.*, 76 (I), 409 (1899).
[83] F. M. Litterscheid, *Ann.*, 315, 187-189 (1901).
[84] R. C. Huston and D. T. Ewing, *J. Am. Chem. Soc.*, 37, 2394-2399 (1915).

forter and Kokatnur. According to Huston and Ewing, it is possible to obtain polynuclear compounds containing as high as four benzene rings connected by CH_2 groups. The formation of these compounds was assumed by them to be due to the fact that the trioxymethylene had decomposed into formaldehyde under the reaction conditions, and that the active reagent in the reaction is formaldehyde, and not molecular trioxymethylene.

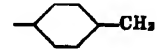
In subsequent polemical papers [85] it was decided that, in the reaction of trioxymethylene on benzene with aluminum chloride, the reacting agent may be formaldehyde, but that since nothing was known of the action of formaldehyde on benzene with aluminum chloride this conclusion could be only an assumption.

The polynuclear compounds secured by Huston and Ewing from xylene were assigned the general structure:



The corresponding tetramer, as well as isomers of the trimer and tetramer, was also thought to be present. The formation of these compounds may be explained by the assumption of intermediate formation of dimethyl benzyl chlorides [86] from dichloromethyl ether and *p*-xylene, and subsequent addition of the dimethyl benzyl chlorides with each other.

The resinification, or polymerization, of benzyl halides and related compounds is well known. In 1932 Jacobson [87] reviewed the work which has been done in this field and made an investigation of polymers obtained from benzyl chloride, *p*-bromobenzyl chloride, and p-xylylene bromide. From a study of the properties of the polymers, he assumed that they are hydrocarbon chains containing the group

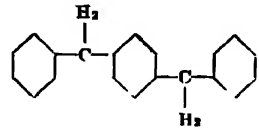


as the structural unit. Since this is the kind of structure assigned by Huston and Ewing to the product of the reaction of trioxymethylene with *p*-xylene and aluminum chloride, it may be assumed that the reaction goes through the formation of xylyl chloride.

In this connection it is interesting that various workers have reported the condensation of benzene homologs with formaldehyde in the presence of sulfuric acid to give diarylmethanes, alkylated benzenes, and polynuclear hydrocarbons,[88] and that *p*-dibenzylbenzene has been reported as

[85] G. B. Frankforter and V. R. Kokatnur, *J. Am. Chem. Soc.*, **37**, 2399-2401 (1915). R. C. Huston and D. T. Ewing, *ibid.*, **37**, 2401 (1915).
[86] *cf.* F. M. Litterscheid, *loc. cit.*
[87] R. A. Jacobson, *J. Am. Chem. Soc.*, **54**, 1513-1518 (1932).
[88] A. Nastjukoff, *J. Russ. Phys.-Chem. Soc.*, **35**, 824-831 (1903); *C. Z.*, 1903 II, 1435.

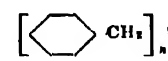
one of the products of the condensation of formaldehyde and benzene with concentrated sulfuric acid in acetic acid.[89] The structure of *p*-dibenzyl benzene



resembles greatly the structures of the products obtained by Huston and Ewing.

The production of anthracene or anthracene derivatives in the reaction of trioxymethylene with aromatic hydrocarbons and aluminum chloride may also be traced through the intermediate formation of aralkyl halides. Benzyl chloride, for example, has been shown to condense with itself in the presence of aluminum chloride to give anthracene.[90]

Since diphenylmethane, polynuclear hydrocarbons of the type



and anthracene are all products derived from benzyl chloride, it and related compounds may be assumed to be intermediate products in the reaction of trioxymethylene with aromatic hydrocarbons and anhydrous aluminum chloride. The formation of benzyl chloride may be caused by intermediate formation of dichlorodimethyl ether from trioxymethylene and hydrogen chloride. Since trioxymethylene is known to contain up to 7 per cent of water, the hydrogen chloride necessary may easily be produced by the action of this water content on the anhydrous aluminum chloride.

The role of hydrogen chloride in this reaction has been recognized by Bodendorf,[91] who prepared diaryl paraffins by addition, at 0°, of 1 mole of an aliphatic aldehyde to a suspension of 1.2 moles of aluminum chloride in a large excess of benzene saturated with dry hydrogen chloride. From the appropriate aldehydes he secured 50 per cent yields of 1,1-diphenylethane, -*n*-propane, and -*n*-butane, and 1,1-diphenyl-2-methyl-*n*-propane. By-products were alkylbenzenes and resinous materials.

The action of anhydrous aluminum chloride and trioxymethylene on naphthenes has been studied.[92] Cyclohexane and methylcyclohexane, which do not react with formalin, were found to react with trioxymethylene and anhydrous aluminum chloride to give a mixture of hydrocarbons. One of the products was probably hexamethylbenzene. The main fraction, boiling at 212-215°, contained 1 per cent of oxygen from which the hydrocarbon could not be freed. Its boiling range indicated that it might be

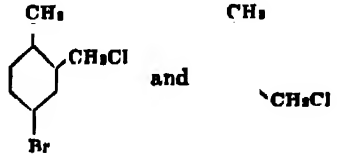
[89] J. Thiele and H. Balhorn, *Ber.*, 37, 1463-1470 (1904).
[90] J. Lavaux and M. Lombard, *Bull. soc. chim. (4)*, 7, 539-542 (1910); *C. A.*, 4, 2448.
[91] K. Bodendorf, *J. prakt. chem. (2)*, 129, 327-339 (1931); *Brit. Chem. Abs.-A*, 934 (1931).
[92] A. Nastjukoff and N. Gurin, *J. Russ. Phys.-Chem. Soc.*, 47, 46-52 (1915); *C. Z.*, 1916 I, 700.

naphthalene, but it would not react with formaldehyde and sulfuric acid Upon purification by recrystallizing from alcohol and ether an oxygenated compound was obtained. Upon distillation of the material remaining in the mother liquor, however, a substance was again obtained which would not react with formaldehyde and sulfuric acid, and still was not free of oxygen. The constitution of this product was not further investigated, but it was assumed to be a product of the reaction of polymethylene glycol with cyclohexane or an aromatic hydrocarbon, the oxygen present being chemically bound as stable ether oxygen.

On the whole, the reaction of cyclohexane with trioxymethylene and aluminum chloride was found to be complicated, simultaneous dehydrogenation and condensation occurring.

A reaction which is generally used today for the preparation of aromatic chloromethyl derivatives is traceable to the work of Grassi-Cristaldi and Maselli,[92] who found that if the reaction product of hydrogen chloride and paraformaldehyde is treated with benzene and zinc chloride in carbon disulfide, benzyl chloride is formed. The reaction was subsequently investigated by Litterscheid,[93] and more recently by Blanc,[94] who found that by the action of hydrogen chloride on various aromatic hydrocarbons in the presence of trioxymethylene or formalin and powdered zinc chloride it was possible to get good yields of their chloromethyl derivatives. Thus with benzene he obtained an 80 per cent yield of benzyl chloride, together with some *p*-bis-(ω-chloromethyl)benzene. He found the reaction similarly applicable to the preparation of chloromethyl derivatives of toluene, *m*-xylene, ethylbenzene, propylbenzene, cymene, and naphthalene, though smaller yields of monosubstituted products were obtained from these compounds.

Blanc's reaction has been applied recently to synthesis of chloromethyl derivatives of *p*-bromomethyl (or ethyl) benzene, intermediates in the preparation of carcinogenic hydrocarbons. Blanc's method has been somewhat modified in that a special catalyst, consisting of a 10:1 mixture of zinc chloride and aluminum chloride, is used. In the preparation of chloromethyl derivatives of *p*-bromotoluene, Fieser and Seligman [95] report that the yield was increased about threefold by the use of this special catalyst. A 74 per cent yield of a mixture of the two chloromethyl derivatives,



was thus obtained.

[92] F. M. Litterscheid, *Ann.*, 316, 127-139 (1901).
[93] G. Blanc, *Am. Perfumer*, 17, 541-543; *C. A.*, 17, 1690; *Bull. soc. chim.* 33, 313-319 (1923).
[94] L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, 57, 942-946 (1935).

Similarly, a 76 per cent yield of chloromethyl derivatives of *p*-bromoethylbenzene has been reported.[96] A 69 per cent yield of a mixture of 2- and 3-chloromethyl-4-bromo-*tert*-butylbenzene has been secured by treating with dry hydrogen chloride for 18 to 20 hours at 60-70° a mixture of 304 g of *p*-bromo-*tert*-butylbenzene, 43 g of trioxymethylene, and 200 g of zinc chloride which had been freshly fused with 3 g of aluminum chloride.[97]

The production of *o*- or *p*-xylenes by the action of formaldehyde on toluene in the presence of hydrogen chloride and a condensing agent like aluminum chloride, and hydrogenation of the *o*- or *p*-xylyl chlorides thus obtained, has been claimed.[98]

Aluminum chloride has been claimed to be an effective catalyst in the condensation of aliphatic aldehydes with aromatic amines for production of accelerators for the vulcanization of rubber.[99]

Aromatic Aldehydes

Benzaldehyde with benzene in the presence of aluminum chloride has been shown to yield a mixture of diphenylmethane, triphenylmethane, and anthracene.[100] According to Hey,[101] in the production of anthracene derivatives by reaction of aromatic aldehydes with aromatic hydrocarbons and aluminum chloride, only the meso-carbon atoms are supplied by the aldehyde.

The condensation of benzaldehyde with toluene and aluminum chloride at 60° for six hours yields a mixture of 2,6- and 2,7-dimethylnaphthalenes, together with a mixture of 2,6- and 2,7-dimethylanthracenes. When *m*- or *p*-tolualdehyde or *o*-chlorobenzaldehyde was reacted with benzene in the presence of aluminum chloride, the product consisted of anthracene and triphenylmethane, together with toluene and *m*-xylene, in the reaction with the tolualdehydes, and chlorobenzene in the reaction with *o*-chlorobenzaldehyde. 2-Furaldehyde and toluene with aluminum chloride gave a mixture of dimethylanthracenes. These observations indicate that the nucleus to which the aldehyde group is attached plays no part in building up the anthracene molecule. It may be inferred that it is the hydrocarbon nuclei alone which go to form the two end-rings in the anthracene and the rings in triphenylmethane. In the reaction with the tolualdehydes and *o*-chlorobenzaldehyde, the formation of toluene, *m*-xylene, and chlorobenzene points to cleavage of the carbonyl group from the aldehyde. That aluminum chloride effects decomposition of benzaldehyde into benzene and carbon monoxide was confirmed experimentally.[101] That the dimethylanthracenes may have been produced by action of the cleaved carbon monoxide on the hydrocarbon may be assumed from the fact that upon passing carbon monoxide into hot tolu-

[96] W. F. Bruce and S. J. Kahn, *J. Am. Chem. Soc.*, 60, 1017-1019 (1938).
[97] L. F. Fieser and D. K. Snow, *J. Am. Chem. Soc.*, 60, 176-177 (1938).
[98] French P. 639,252 to Gen. Aniline Works; *C. A.*, 23, 611 (1929).
[99] U. S. P. 1,754,010 (1930) to A. Cambron (to Roessler and Hasslacher Chemical Co.), *Brit. Chem. Abs.*-B, 993 (1930); U. S. P. 1,858,577 (1932) to A. Cambron (to Roessler and Hasslacher Chemical Co.).
[100] A. Schaarschmidt, L. Hermann, and B. Zsemso, *Ber.*, 58, 1914-1916 (1925), *C. A.*, 20, 587.
[101] D. H. Hey, *J. Chem. Soc.*, 72-75 (1935); *C. A.*, 29, 1785.

ene containing aluminum chloride, there is secured a mixture of 2,6- and 2,7-dimethylanthracenes in a much better yield than that previously secured [102] from the action of aluminum chloride alone on boiling toluene.

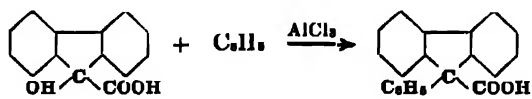
Continuing the investigation, the xylenes and biphenyl were reacted with benzaldehyde in parallel experiments.[103] With all three xylenes, benzaldehyde and aluminum chloride gave tetramethylanthracenes. Biphenyl in carbon disulfide was reacted with benzaldehyde or with methylene dichloride in presence of aluminum chloride. From both reactions, a mixture of 2,6- and 2,7-diphenylanthracenes was obtained. These experiments further confirm the view that benzaldehyde serves only to supply the meso-carbon atoms in anthracene.

Miscellaneous Dehydrating Reactions

Dehydration of benzamide to benzonitrile occurs upon distillation of these materials with a molecular equivalent of aluminum chloride to give an 84 per cent yield of the nitrile. Similar treatment of ammonium benzoate, using 2 molecular equivalents of aluminum chloride, gives a 50 per cent yield of benzonitrile. The reaction has been also applied to chloro- and nitro- derivatives of benzamide and to 1- or 2-naphthamide.[104]

The action of aluminum chloride on phenol at 350° results in the formation of diphenyl ether among other products.[105] When cresol is boiled with 10 per cent of anhydrous aluminum chloride, there is secured 3,6-dimethylxanthene in 5 per cent yield, together with *m*-cresyl ether.[106]

When diphenyleneglycolic acid is reacted with benzene and aluminum chloride, condensation occurs with cleavage of water [107]:



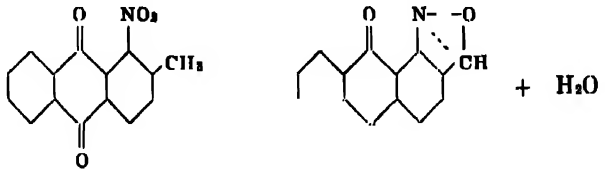
The direct production of aromatic amines by treatment of an aromatic hydrocarbon with hydroxylamine in the presence of aluminum chloride has been reported.[108] Aniline is produced in small quantities from ben-

zene, toluene gives a mixture of *o*- and *p*-toluidines, and *o*-xylene gives a relatively good yield of 4-amino-1,3-xylene. Similar condensations with *p*-xylene, mesitylene, and naphthalene are described. An attempt

[102] R. Anschütz and H. Immendorff, *Ber.*, 17, 2816-2817 (1884); 18, 657-662 (1885).
[103] H. Ellison and D. H. Hey, *J. Chem. Soc.*, 1847-1853 (1938).
[104] J. F. Norris and B. M. Sturgis, *J. Am. Chem. Soc.*, 61, 1413-1417 (1939). J. F. Norris and J. Klemka, *ibid.*, 62, 1432-1435 (1940).
[105] V. Meyer and W. Wurth, *Ber.*, 14, 187-202 (1881); *J. Chem. Soc. Abs.*, 264 (1881).
[106] J. Postowsky and B. Lugowkin, *J. prakt. Chem. (2)*, 122, 141-146 (1929); *Brit. Chem. Abs.*-A, 925 (1930).
[107] D. Vorländer and A. Pritzsche, *Ber.*, 46, 1793-1796, *C. A.*, 7, 1913.
[108] C. Graebe, *Ber.*, 34, 1775-1781 (1901); *J. Chem. Soc. Abs.*, 80 (I), 533 (1901).

was made to substitute phenyl- or *p*-tolylhydroxylamine or benzophenone oxime for hydroxylamine in the reaction with benzene, but no appreciable yields of condensation products were secured. It was later shown, however, that phenylhydroxylamine does condense with benzene with formation of *p*-aminobiphenyl, because of a dehydrogenating condensation.[109]

1-Nitro-2-methylanthraquinone is converted into anthraquinone-1,2-isoxazole upon treatment with aluminum chloride[110]:

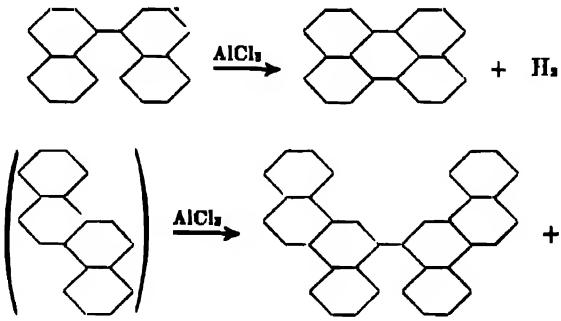


[109] A. Kliegl and H. Huber, *Ber.*, **53**, 1646-1655 (1920)
[110] German P. 479,350 to I. G.

Chapter 13

Dehydrogenating Condensations and Reduction Phenomena

Aluminum chloride catalyzes nuclear dehydrogenation condensation of aromatic hydrocarbons, with formation of higher ring compounds. The reaction may be intramolecular or intermolecular. Thus 1,1′-binaphthyl yields perylene,[1] and two moles of chrysene yields 2,2′-bichrysenyl [2]:



Dehydrogenating condensations of this type have been frequently mentioned in the literature as side reactions observed upon treatment of aromatic hydrocarbons with aluminum chloride. Often apparent during alkylation, they have been generally considered only as obstacles which prevented smooth Friedel-Crafts reaction. Numerous illustrations of such condensations are given in that section of this book which deals with the effect of aluminum chloride on aromatic hydrocarbons.* Hence, in order to avoid repetition, the discussion which follows will be limited to reactions involving dehydrogenating condensations of compounds other than aromatic hydrocarbons.

Since the application of the dehydrogenating activity of aluminum chloride to the synthesis of polynuclear ring systems has been largely worked out by Scholl, who has extended it primarily to the synthesis of a wide range of oxygenated derivatives, condensations of this type are known as Scholl reactions. The method offers a means for the preparation of a wide series of polynuclear compounds having quinoid radicals, and hence has been extensively used in the manufacture of dyestuffs. In many cases the use of an oxidative mixture of fused $AlCl_3$-NaCl removes the hydrogen more effectively. This process is advisable in certain cases

[1] R. Scholl, C. Seer, and R. Weitzenbock, *Ber*, 43, 2202-2209 (1910); Brit. P. 425,363 (1933) to I. G.; *Brit. Chem. Abs.*-B, 443 (1935).

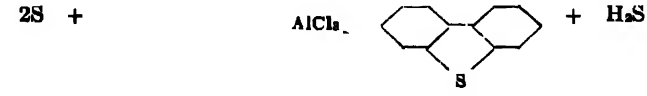
[2] French P. 795,447 (1936) to I. G.; *C. A.*, 30, 5895; German P. 638,485 (1936) to I. G.; *C. A.*, 31, 1040.

* See page 712.

where the evolved hydrogen has a tendency to reduce ketonic groups to hydroxyl groups.

The fate of the hydrogen evolved in such condensations is of interest. The catalytic hydrogenating action of aluminum chloride is discussed in this chapter. For example, when nitrobenzene is boiled with benzene and aluminum chloride, a small yield of *p*-aminobiphenyl is obtained.

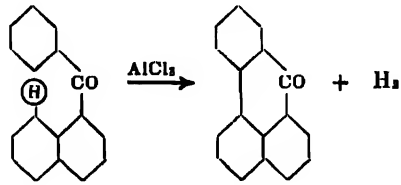
Aluminum chloride also acts as a dehydrogenating catalyst in reactions of sulfur with aromatic compounds, for example in the preparation of dibenzothiophene from biphenyl and sulfur:



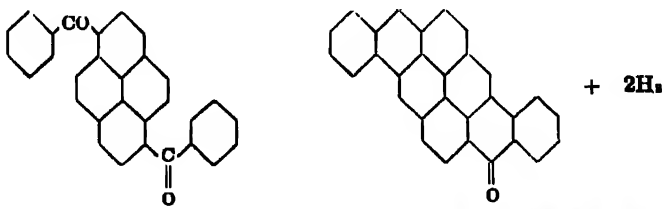
Intramolecular Condensations

Scholl Reaction

Polynuclear Ketones.—In polynuclear ketones the hydrogen which is in the *peri*-position to the carbonyl group is caused to become sufficiently labile by the action of aluminum chloride at high temperatures to permit ring closure at the *peri*-position:

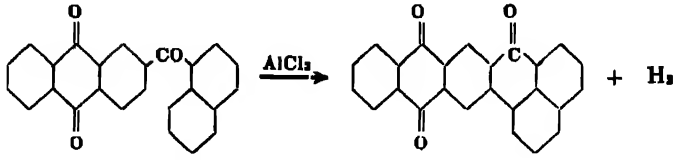


Scholl and Seer[3] have attempted, without success, the preparation of fluorene by heating benzophenone with aluminum chloride. Polynuclear hydrogen is obviously more readily set free than is benzenoid hydrogen. The preparation of 1,9-benzanthrone from phenyl 1-naphthyl ketone, noted above, was effected in a 76 per cent of theoretical yield by heating the ketone with 5 parts of aluminum chloride at 150° for 2½ hours. These investigators[4] applied analogous procedure for the intramolecular ring closure of a miscellany of polynuclear ketones. 1,1′-Dinaphthyl ketone was found to yield naphthabenzanthrone. Dibenzoylpyrene gave pyranthrone:

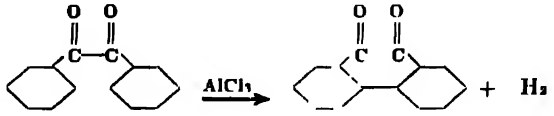


[3] R. Scholl and C. Seer, *Ann.*, 394, 111-177 (1912); *J. Chem. Soc. Abs.*, 104, 56 (1913).
[4] R. Scholl and C. Seer, *loc. cit.*; *Monatsh.*, 33, 1-8 (1912), *C. A.*, 6, 999; German P. 239,701 (1911) to R. School, *J. Chem. Soc. Abs.*, 102 (I), 195 (1912).

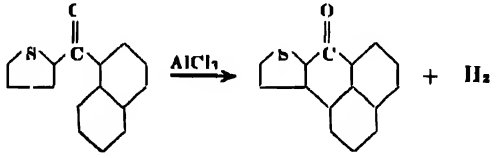
2-Anthraquinoyl 1-naphthyl ketone produced 9,10-phthaloylbenzanthrone:



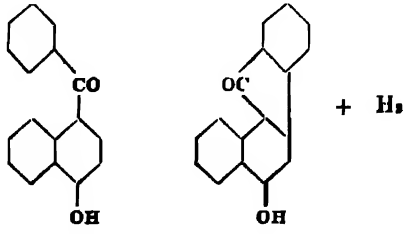
Benzil formed phenanthrenequinone:



2-Thienyl 1-naphthyl ketone was converted to benzthiophanthrone-9:

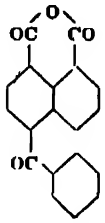


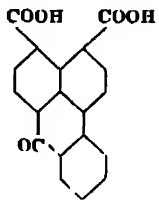
The reaction has been extended to hydroxy-, alkoxy-, or carboxy-derivatives of aroyl ketones. Thus phenyl 2,3-dihydroxy-1-naphthyl ketone gives the expected 5,6-dihydroxy-1,9-benzanthrone.[5] With 4-hydroxy or 4-methoxy-1-benzoylnaphthalene, however, five-membered ring closure, with formation of 6-hydroxy-7,8-benzofluorenone, occurs[6]:



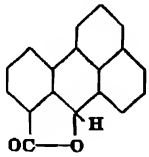
3,9-Di-*p*-methoxybenzoylperylene has been reported to yield a mixture of dimethoxy- and dihydroxyisoviolanthrones.[7] Benzanthrone *peri*-dicarboxylic acid or its derivatives may be secured by heating 4-benzoyl-1,8-naphthalic anhydride or its substitution products with aluminum chloride with or without an oxidizing agent[8]:

[5] J. Turski and J. Grynwasser, *Roczn. Chem.*, **9**, 78-82 (1929)
[6] H. E. Fierz-David, *Helv. Chim. Acta.*, **11**, 1046 (1928); Swiss P. 133,319 (1937), and U. S. P. 2,090,488 (1937) to Soc. pour l'Ind. Chim.; *C. A.*, **31**, 6998, 7200.
[7] Russian P. 51,427 (1937) to A. M. Lukin; *C. A.*, **33**, 7126.
[8] German P. 494,111 (1927) to G. Kranzlein, H. Greune, and H. Vollmann (to I. G.), *C. A.*, **24**, 2757; Brit. P. 283,985 (1928) to I. G., *Brit. Chem. Abs.*-B, 748 (1929).

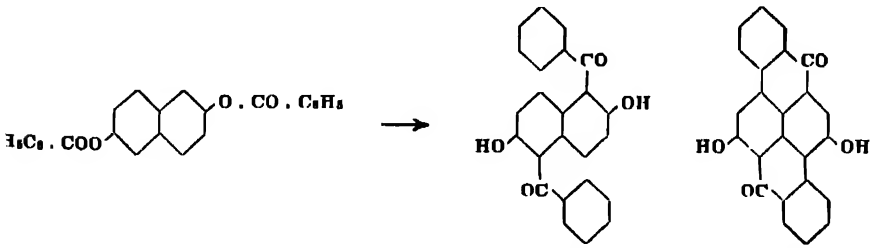




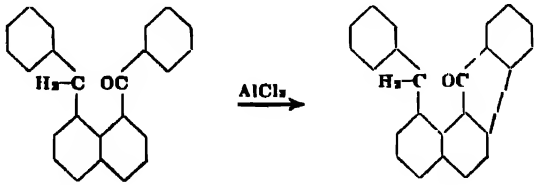
o-α-Naphthoylbenzoic acid is converted by fusion in an $AlCl_3$-NaCl melt at 100° into a product which probably has the following structure [9]:



The formation of polynuclear compounds through ketones may also be effected from benzoates, which give hydroxy- ketones by Fries migration.[10] 2,6-Naphthyl dibenzoate undergoes the following series of conversions in the presence of aluminum chloride:



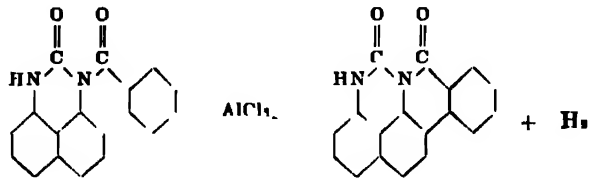
The reaction with 1-benzoyl-8-benzylnaphthalenes is of interest in that ring closure occurs with formation of a five-membered ring [11]:



Here the presence of a substituent in the *peri*-position makes the formation of a six-membered ring impossible. With 1-benzoyl-4-benzylnaphthalene, condensation takes the usual course, with production of 4,5,8,9-dibenzo-10-keto-3-hydropyrene.

[9] British P. 303,375 (1928) to I. G.; *Brit. Chem. Abs.*-B, 706 (1930).
[10] German P. 555,955 and 453,280 to I. G. Farbenindustrie.
[11] K. Dziewonski and J. Mossew, *Roczn. Chem.*, 11, 189-192 (1931); *Brit. Chem., Abs.*-A, 732 (1931).

When N-benzoylperimidone is heated at 150-170° with sodium aluminum chloride, or is boiled in carbon disulfide with aluminum chloride, intramolecular condensation occurs according to the scheme [12]:



Similar products are secured from the *m*-nitrobenzoyl and α-naphthoyl derivatives.

The use of aluminum chloride as an oxidizing catalyst was noted by Friedel and Crafts,[13] who found that upon passing moist air through a mixture of benzene and aluminum chloride, some oxygen is fixed, resulting in the formation of phenol and other oxygen derivatives. They assumed the following mechanism:

$$C_6H_6 \xrightarrow{Al_2Cl_6} C_6H_6 . Al_2Cl_6 \qquad C_6H_5O . Al_2Cl_5 \xrightarrow{H_2O} C_6H_5OH + (OH)Al_2Cl_5$$

More recently the production of phenols has been noted during studies on the effect of aluminum chloride on aromatic hydrocarbons * and it has been suggested as a catalyst for oxidation of hydrocarbon oils.[14] Very low concentrations of aluminum chloride have been found to activate the oxidative deamination of glycine.[15]

Since the Scholl reaction is one of dehydrogenation, the use of an oxidative mixture of fused salts, or of an oxidizing agent together with aluminum chloride, has been found effective in accelerating condensation The aroyl hydrocarbons used in these syntheses are ordinarily prepared by reaction of an aroyl chloride with the appropriate aromatic compound in presence of aluminum chloride. When reaction is effected in a fused salt mixture, as for example in an $AlCl_3$-NaCl melt, ring closure may occur during the preparation of the ketone. Dibenzopyrenequinone and its derivatives are thus secured from α-aroylnaphthalenes and aroyl chlorides.[16] Oxidative ring closure offers a method for the preparation of polynuclear products from mixed diketones.[17] Thus, methylpyranthrone is formed by adding benzoylpyrene and *p*-toluyl chloride to an $AlCl_3$-NaCl melt at 110-120°, raising the temperature quickly to 165°, and passing in oxygen until the reaction is complete, the fused mass becoming

[12] U. S. P. 1,749,855 (1930) to W. Miegand and R. Haddenreich (to Gen Aniline Works, Inc.); *Brit Chem., Abs.*-B, 599 (1930).

[13] C. Friedel and J. M. Crafts, *Compt. rend.*, 84, 884-887 (1878); *J. Chem. Soc. Abs.*, 870 (1878), *Bull. soc. chim. (2)*, 29, 99 (1878).

* See Chapter 16.

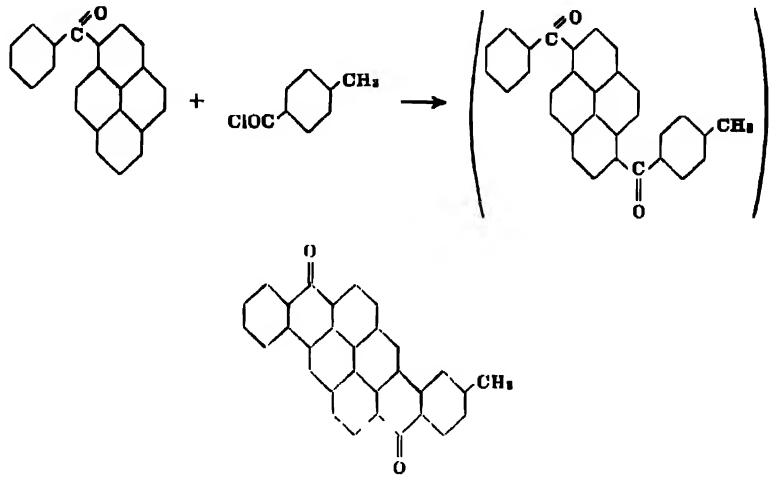
[14] U. S. P. 1,710,155 (1929) to G. Egloff and J. C. Morrell (to Universal Oil Products), *C. A.*, 23, 2830; Brit. P. 441,768 (1936) to J. W. Walt, *C. A.*, 30, 4660.

[15] B. Kisch and K. Schuwirth, *Biochem. Z.*, 268, 158-163 (1934), *Brit. Chem. Abs.*-A, 448 (1934).

[16] German P. 483,288 to I. G. Farbenindustrie.

[17] R. Scholl, K. Meyer, and J. Donat, *Ber.*, 70, 2189-2199 (1937); U. S. P. 2,073,485 (1937) to R. Scholl, K. Meyer, and J. Donat.

blue. Reaction probably occurs according to the following scheme, the indicated intermediate compound not being isolated:



Similar condensations occur between benzoyl pyrene and cinnamoyl chloride and between benzoylpyrene and phthalic anhydride.

Some ring closures of polynuclear ketones are summarized in the following table:

Table 32

Ketone	Added reactant	Product	Ref.
Phenyl 7-alkyl-1-naphthyl ketones		no conversion to benzanthrones	32
o-Tolyl α-naphthyl ketone		5-methyl-1,9-benzanthrone	1
m-Tolyl α-naphthyl ketone		6-methyl-1,9-benzanthrone	1
p-Tolyl α-naphthyl ketone		7-methyl-1,9-benzanthrone	1
o-Tolyl α-naphthyl ketone *p*-Tolyl α-naphthyl ketone		same methylbenzanthrone, probably 8-methyl-1,9-benzanthrone	9
3,8-Di-α-naphthoylpyrene		5,6,5′,6′-dibenzpyranthrone	1
3,8-Di-β-naphthoylpyrene		7,8,7′,8′-dibenzpyranthrone	1
peri-Aroyl derivatives, *e.g.*, 1,8-dibenzoylnaphthalene	aromatic nitro compds. contg. at least 1 other negative substituent	3,4,8,9-dibenzopyrene-5,10-quinone	10, 36
1,4-Dibenzoylnaphthalene		4,5,8,9-dibenzopyrene-3,10-quinone (5%)	4
1,5-Dibenzoylnaphthalene		no reaction	4
1,4- or 1,8-Dibenzoylnaphthalenes	$AlCl_3$ + NaCl or pyrolusite	dibenzopyrenequinones	9
x-Benzoyl-*x*-toluyl pyrene	$AlCl_3$+NaCl +O_2	mono-methylpyranthrone	19
3,9-Dibenzoyl perylene	MnO_2	isoviolanthrone (45%)	6
Dibenzoyl perylenes	MnO_2	condensation products	13
Benzoyl perylenes		perylene dyes	13
3,5,8,10-Tetraroyl pyrenes	NaCl+$AlCl_3$ + O_2	dyes of the pyranthrone series	35
1-Methyl-4-benzoyl naphthalene		4-methyl-*peri*-benzanthrone	3
2-Methyl-1-benzoyl naphthalene		6-methylbenzanthrone	3

Table 32—*(Continued)*

Ketone	Added reactant	Product	Ref.
1-Methyl-4-benzoyl naphthalene		3-methylbenzanthrone	5
2-Methyl-1-benzoyl naphthalene		same as above	5
α,α'-Dinaphthyl ketone	$AlCl_3$+NaCl	1,2,5,10-dibenz-9-anthrone (27%)	17
2-Methyl-1,1-dinaphthyl ketone	$AlCl_3$+NaCl	3-methyl-1,2,5,10-dibenz-9-anthrone violanthrone	18 1
3,4-Dihydroxybenzil		2,4-dihydroxyphenanthrenequinone (migration of hydroxyl?)	26
3,4-Dimethoxybenzil		2,3-dimethoxyphenanthrenequinone	25
o-Methoxybenzil		1-hydroxyphenanthrenequinone	27
Benzil		phenanthrenequinone (25%)	1, 2, 29
Desoxybenzoin		unchanged	2
4-Benzoyl-1-benzyl naphthalene		4,5,8,9-dibenzo-10-keto-3-hydropyrene	8
1-Benzoyl-8-benzyl naphthalene		benzylchrysofluorene, m.p. 167–168°	8
α- or α,α- or α,*meso*-mono- or diaroyl-anthracenes		pyrenequinones and perylenequinones	7
Anthracyl aryl ketone or anthracyl bis-aryl diketone	$AlCl_3$+kiesel-guhr	closed ring compounds	11
Monobenzoylanthrone	NaCl-$AlCl_3$	3,4,8,9-dibenz-pyrene-5,10-quinone	28, 30
Benzoyl-2-aroyl-hydroxybenzanthrones with free *peri*-positions	melted $AlCl_3$	hydroxy-dibenzopyrenequinones	31
3,9-Bis(*p*-methoxybenzoyl)-perylene		mixture of dimethoxyisoviolanthrone and dihydroxyisoviolanthrone; if MnO_2 is used with $AlCl_3$, yield of dimethoxy derivatives is increased, chlorodimethoxyisoviolanthrone is also formed	9
4-Hydroxy-1-benzoylnaphthalene		6-hydroxy-7,8-benzofluorenone	24
2-Hydroxy-3-naphthyl phenyl (or *p*-tolyl) ketone		1-hydroxy-3,4-benzofluorenone	14, 33
3-Hydroxy-2-naphthyl phenyl ketone or 3-hydroxy-2-naphthyl *p*-tolyl ketone		hydroxybenzofluorenones	23
2,3-Dihydroxyphenyl α-naphthyl ketone		5,6-dihydroxy-dihydro-1,9-benzanthrone	15
Phenyl 2,3-dihydroxy-α-naphthyl ketone		3,4-dihydroxy-1,9-benzanthrone	15
4-Benzoyl-1,8-naphthalic anhydride	with or without an oxidizing agent	benzanthrone-3,4-dicarboxylic acid	20, 21
α,α,β-Triphenylpropionic acid	$AlCl_3$+little H_2O	9-phenyl-9,10-dihydrophenanthrene-10-carboxylic acid	22
α-Naphthyl *o*-chlorophenyl ketone		no reaction	16
α-Naphthyl *m*- or *p*-chlorophenyl ketones		6- or 7-chlorobenzanthrones, respectively; yields much smaller than that of benzanthrone secured from non-chlorinated ketones	

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3. F. Mayer and A. Sieglitz, *Ber.*, 55, 1835-1859 (1922); *C. A.*, 17, 99.
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22. J. C. Earl and W. A. Kable, *Chem. and Ind.*, 475 (1934); *C. A.*, 29, 2162.
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31. U. S. P. 1,693,447 (1929) to G. Kranzlein, K. Zahn, P. Ochwat, and M. Corell (to Grasselli Dyestuff Corp.); *C. A.*, 23, 715.
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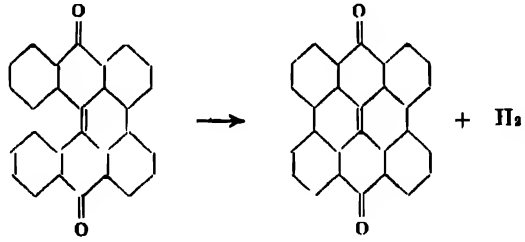
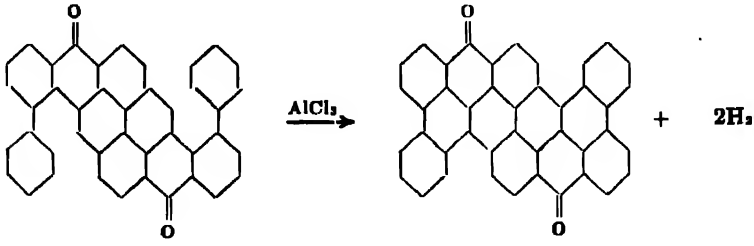
35. German P. 654,515 (1937) to I. G.; *C. A.*, 32, 3625.
36. U. S. P. 2,238,180 (1941) to E. Moergeli, K. Krauer, and M. Bommer (to Soc. Chem. Ind. in Basle.

Miscellaneous Intramolecular Condensations

In 1910, Scholl and Mansfeld[18] observed that *meso*-benzodianthrone was converted to *meso*-dinaphthodianthrone upon treatment with aluminum chloride:

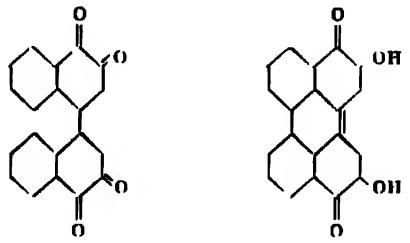


5,13-Diphenylpyranthrone, upon treatment with aluminum chloride followed by air-oxidation, is converted into a bright orange vat dye, probably according to the scheme[19]:

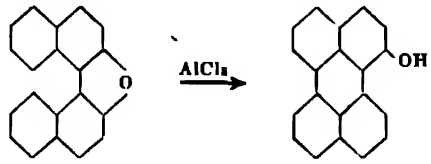


1,1′-Binaphthyl-3,4,3′,4′-tetraquinone yields 2,11-dihydroxyperylene-3,10-quinone.[20] Here the fate of the hydrogen which is evolved is seen in the production of the hydroxy- derivative:

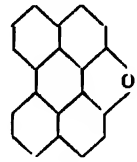
[18] R. Scholl and J. Mansfeld, *Ber.*, 43, 1737-1746 (1910).
[19] British P. 262,639 (1927) to I. G.; *Brit. Chem. Abs.*-B, 517 (1928).
[20] German P. 412,130 to Badische Anilin f. Soda-Fabrik.



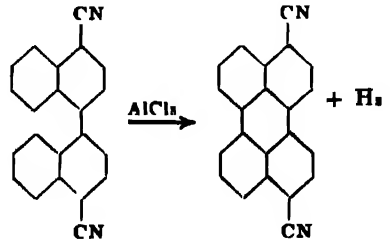
When β-dinaphthalene oxide is melted with aluminum chloride, the five-membered ring is cracked, the hydrogen evolved by nuclear condensation adding at the points of cleavage [21]



The yield of hydroxyperylene thus secured is only about 6 per cent 1,12-Furoperylene,



was also secured from the reaction. 4,4'-Dicyano-1,1'-binaphthyl is converted into 3,10-dicyanoperylene by heating for 1½ hours at 140° with aluminum chloride. From 2.5 g of the binaphthyl there is secured 1 8 g of the perylene derivative [21]:

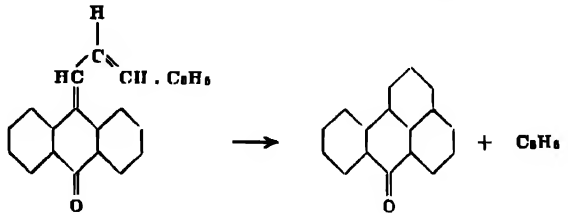


The transformation of 2,2'-dimethoxy-1,1'-binaphthyl into 1,12-dihydroxyperylene by heating with 4 parts of aluminum chloride at 140-150° for two hours has been reported.[22]

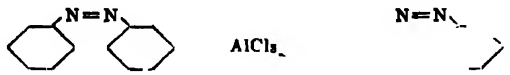
[21] R. Weitzenbock and C. Seer, *Ber.*, 46, 1994-2000 (1913); *J. Chem. Soc. Abs.*, 104 (I), 847 (1913)
[22] A. Zinke and R. Dengg, *Monatsh.*, 43, 125-126 (1922); *J. Chem. Soc. Abs.*, 122 (I), 1013 (1922)
Brit. P. 165,771 to A. Zinke, *J. Chem. Soc. Abs.*, 122 (I), 183 (1923).

According to Corbellini and Aymar,[23] the condensation of β-dinaphthol to dihydroxyperylene takes place in the presence of aluminum chloride alone, but scanty yields are obtained.

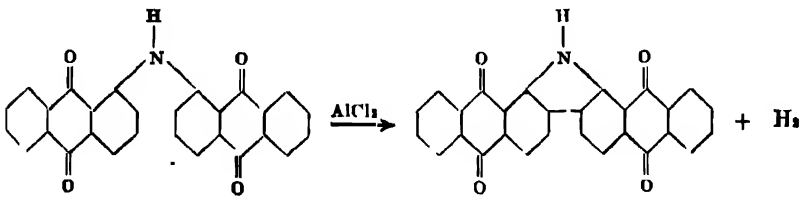
The ring closure of cinnamylidenanthrone does not occur merely by addition at the double bond. Instead, the phenyl residue is cracked off as benzene, condensation taking place by dehydrogenation[24]:



Azobenzene undergoes intramolecular closure when heated with aluminum chloride to yield phenazone[25]:



Anthrimides undergo dehydrogenation with formation of carbazole dyestuffs[26]:

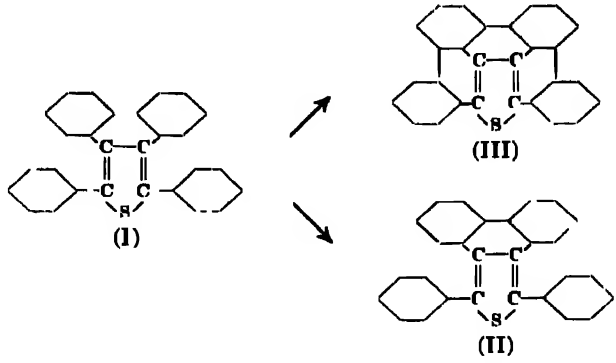


The addition compound of pyridine with aluminum chloride has been suggested as an excellent condensing agent for effecting ring closure of dianthraquinonylamines.[27] Cyclization of 4,5'-dibenzamido-1,1'-dianthraquinoylamine has been claimed to take place with less formation of by-products if the aluminum chloride is used as a condensation catalyst in conjunction with an acid halide capable of forming molecular compounds with it. The use of acetyl or benzoyl chloride is mentioned.[28]

Upon heating tetraphenylthiophene (I) with 4 times its weight of aluminum chloride at 115-120° for 40 minutes, it is converted into a mixture

[23] A. Corbellini and G. Aymar, *Giorn. Chim. Ind. Appl.*, 10, 196-199 (1928); *Brit. Chem. Abs.*-B, 396 (1928).
[24] German P. 488,606 to I. G.; Brit. P. 297,129 (1928) to I. G.; *Brit. Chem. Abs.*-B, 847 (1928).
[25] German P. 512,906 to I. G. Farbenindustrie.
[26] German P. 240,930, 251,021, and 267,532 to Farbwerke Meister, Lucius, and Bruning, *J. Chem. Soc. Abs.*, 104 (I), 106 (1913); German P. 520,849 (1930) to I. G.; *C. A.*, 30, 6207.
[27] Brit. P. 297,129 (1927) to I. G.; *Brit. Chem. Abs.*-B, 848 (1928).
[28] British P. 461,422 (1935) to I. G.; *Brit. Chem. Abs.*-B, 532 (1937).

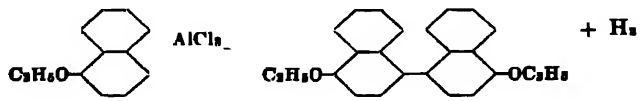
of dehydro-α-diphenanthrenothiophene (III) (m.p. 391-392°) and 2,5-diphenyl-3,4-phenanthrenothiophene (II) (m.p. 260°) in low yields.[29]



Intermolecular Dehydrogenation

Autocondensation

Autocondensation of aromatic hydrocarbons has been included in that section of this book which deals with the effect of aluminum chloride on aromatic hydrocarbons.* Scholl and Seer[30] have found that phenol and naphthol ethers lend themselves much better than the parent hydrocarbons to condensations of the aromatic nucleus by elimination of aromatically bound hydrogen by means of aluminum chloride. The reaction was found to be best effected in nitrobenzene solution; the solvent seeming to prevent cleavage of the alkoxy- groups. From 10 g of α-ethoxynaphthalene in nitrobenzene with 10 g of aluminum chloride they secured after 16 hours 7 g of 4,4′-diethoxy-1,1′-binaphthyl:



Intramolecular condensation of hydroxybinaphthyls obtained by the action of aluminum chloride on hydroxylated derivatives of naphthalene in the presence of aluminum chloride may be secured by heating them with sulfur and sodium sulfide.[31]

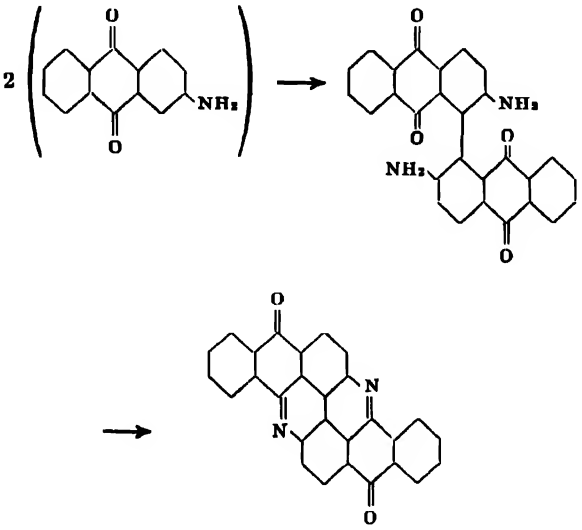
The dihydroxyperylene secured by heating β-binaphthol with aluminum chloride may be converted into 1,12-perylenequinone by treating it with aqueous sodium hydroxide containing aluminum powder.[32]

If manganese dioxide is used with aluminum chloride in the conversion of binaphthol, and the product is purified by boiling with 5 per cent

[29] W. Steinkopf, *Ann.*, 519, 297-300 (1935).
* See Chapter 16.
[30] R. Scholl and C. Seer, *Ber.*, 55, 330-341 (1922), *C. A.*, 16, 1505.
[31] Brit. P. 212,886 (1923) to Compagnie Nationale de Matières Colorantes et de produits Chimiques, *C. A.*, 18, 2254.
[32] A. Zinke and F. Hanselmayer, *Monatsh.*, 46, 231-234 (1925); *J. Chem. Soc. Abs. (I)*, 864 (1925); Brit. P. 165,770 to A. Zinke; *J. Chem. Soc. Abs. (I)*, 122 (1923).

aqueous chromic oxide, perylenequinone is secured directly, α-binaphthol thus yielding perylene-3,10-quinone.[33]

α-Hydroxyanthraquinone is converted into 1,1′-dihydroxybianthraquinonyl by heating it at 100-130° with aluminum chloride in dry pyridine.[34] The formation of flavanthrone from 2 moles of β-aminoanthraquinone involves both dehydrogenation and condensation of amino groups with carbonyl groups with water cleavage.[35] It has been established [36] that 2,2′-diamino-1,1′-bianthraquinonyl is first formed, and this is converted into flavanthrone at 250°:



When dimethylaniline is heated with aluminum chloride in the presence of air, the following condensation occurs [37]:

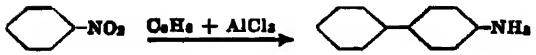
$$2C_6H_5N(CH_3)_2 \qquad (CH_3)_2NC_6H_4 \cdot C_6H_4 \cdot N(CH_3)_2 + H_2$$

Reduction: Fate of Hydrogen Evolved in Dehydrogenating Condensations

Various examples of reduction of compounds containing hydrogen acceptors confirm the evolution of hydrogen effected by action of aluminum chloride on aromatic compounds. The fate of the hydrogen evolved is definitely shown.

When nitrobenzene is boiled with benzene and aluminum chloride there is formed, in addition to much resinous matter, an 8.5 per cent yield of *p*-aminobiphenyl [38]:

[33] A. Zinke, F. Stimler, and E. Reuss, *Monatsh.*, 54, 415-425 (1934); *C. A.*, 29, 1413.
[34] Brit. P. 310,353 (1928) to I. G.; *Brit. Chem. Abs.*-B, 637 (1929).
[35] R. Scholl, *Ber.*, 40, 1691-1702 (1907).
[36] R. Scholl and O. Duchendorfer, *Ber.*, 51, 452-458 (1918).
[37] H. Giraud, *Bull. soc. chim.* (3), 1, 691-695 (1889).
[38] M. Freund, *Monatsh.*, 17, 395-400 (1896); *J. Chem. Soc. Abs.*, 72 (I), 88 (1897).



Since the same compound is formed from phenyl hydroxylamine and benzene in the presence of aluminum chloride,

the hydroxylamine may be assumed to be an intermediate product in the reaction with benzene.[39] Here the hydrogen evolved by condensation of the benzenoid compound to a biphenyl derivative, as well as the hydrogen produced during formation of the resinous mass, served to convert the nitrobenzene into a hydroxylamine and then to amine.

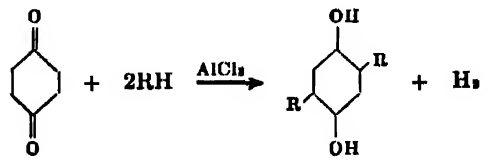
The dehydrogenating effect of aluminum chloride in benzene was subsequently demonstrated by conversion of azobenzene into *p*-aminobiphenyl in 70-80 per cent yields.[40] The following steps were shown to occur in the conversion, hydrogenation and dehydrogenation playing an important part in each step:

$$C_6H_5.N:N\ C_6H_5 + C_6H_6 \longrightarrow C_6H_5.NH.NH.C_6H_4.C_6H_5 \longrightarrow$$
$$C_6H_5.N:N.C_6H_4.C_6H_5 \xrightarrow{C_6H_6} (C_6H_5C_6H_4NH)_2 \longrightarrow 2C_6H_5.C_6H_4NH_2$$

Here the various products obtained were well denoted by color changes; since the reducible compounds were colored, their hydrogenation could be conveniently followed.

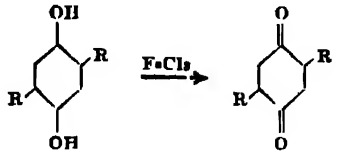
Reduction in Synthesis of Diarylquinones

Diaryl hydroquinones are readily obtained by treatment of *p*-benzoquinone with aromatic hydrocarbons, phenols, or phenol ethers in the presence of aluminum chloride. The quinone group serves as acceptor for part of the hydrogen evolved.

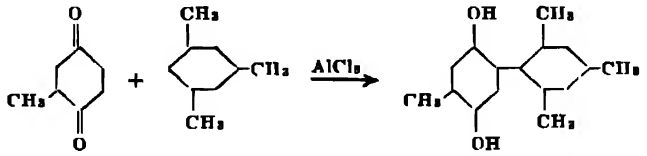


Monosubstitution does not occur. The 2,5-diarylhydroquinones are easily converted into the corresponding quinones upon oxidation with ferric chloride in acetic acid:

[39] A. Kluegel and H. Huber, *Ber.*, 53, 1646-1655 (1920); *J. Chem. Soc. Abs.*, 118, 835 (1920).
[40] R. Pummerer and J. Binapfl, *Ber.*, 54, 2768-2784 (1921); *C. A.*, 16, 1408. *Cf.* E. Bandrowski and A Prokopecko, *Bull. Acad. Sci. Cracow*, 158-182 (1904); *J. Chem. Soc. Abs.*, 86 (I), 638 (1904).



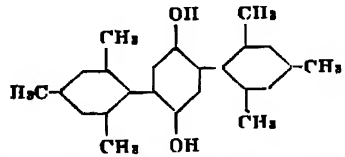
Monoaryl hydroquinones may be prepared by reaction of certain monosubstituted quinones with aromatic hydrocarbons and aluminum chloride. Thus toluquinone and mesitylene gives a 60 per cent yield of 2-(2′,4′,6′-trimethylphenyl)-5-methylhydroquinone [41]:



The aluminum chloride-catalyzed addition of aromatic compounds to quinone was first reported by Pummerer and Prell,[42] who describe the reaction of *p*-benzoquinone with benzene, toluene, phenol, and anisole. The substituted benzenes were found to be more active than benzene itself. Whereas benzene gave only a very small yield of 2,5-diphenyl hydroquinone, treatment of 21.6 g of quinone in 150 cc of toluene with 67 g of aluminum chloride at 0° during one hour and subsequent stirring for four hours gave 20.2 g of crude 2,5-di-*p*-tolylhydroquinone. The product was secured in two forms, one yellow and the other red, which were crystallographically different, but showed the same chemical properties. The addition of anisole or phenol was effected in carbon disulfide solution; the products were 2,5-bis(4′-methoxyphenyl)hydroquinone and 2,5-bis(4′-hydroxyphenyl)hydroquinone, respectively.

Subsequent investigation [43] showed the reaction to be likewise applicable to phenetole, with production of the corresponding *p,p′*-diethoxy compound. Addition of *p*-xylene to benzoquinone was found not to be so readily effected as the analogous reaction with toluene. The structure of the 2,5-dixylylhydroquinone secured was not determined.

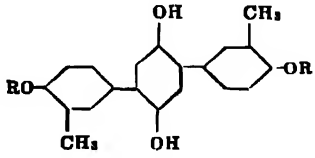
Browning and Adams [44] report a 43.7 per cent yield of 3,6-bis-(2′,4′-dimethylphenyl)-hydroquinone from the reaction of 375 cc of *m*-xylene and 70 g of benzoquinone in the presence of 140 g of aluminum chloride at 20° for two hours. The preparation of 2,5-dimesitylhydroquinone,



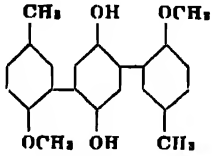
[41] D. W. Hill and R. Adams, *J. Am. Chem. Soc.*, 53, 3452-3461 (1931).
[42] R. Pummerer and E. Prell, *Ber.*, 55, 3105-3116 (1922).
[43] R. Pummerer and H. Fiedler, *Ber.*, 60, 1439-1442 (1927).
[44] E. Browning and R. Adams, *J. Am. Chem. Soc.*, 52, 4093-4107 (1930).

has been effected by using an even greater excess of aluminum chloride. To a mixture consisting of 150 g of aluminum chloride in 700 cc of mesitylene, 50 g of benzoquinone was gradually added at below 5°. Subsequent stirring of the reaction mixture for three hours and customary isolation of the product gave 42 g of the diaryl hydroquinone.[45]

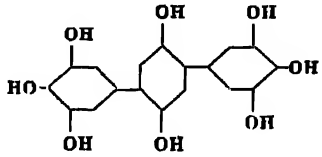
Investigation of the reaction with phenols [46] shows that the position of the substituents has a decided influence on the reactivity of a phenol *o*-Cresol and its ethyl ether readily give 2,5-di-*o*-cresylhydroquinone or the diethyl ether, respectively:



Reaction with *m*-cresol is much more difficult, and it was not possible to secure any product with *p*-cresol. However, *p*-tolyl methyl ether in carbon disulfide solution gave a satisfactory yield of 2,5-bis(2-methoxy-5-methylphenyl)hydroquinone:

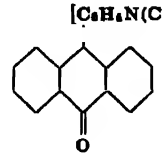


The dihydroxy phenols were also found to have varied reactivity. Resorcinol is especially active, condensing even in the absence of a catalyst,[47] but attempted addition of veratrole or of hydroquinone to benzoquinone in the presence of aluminum chloride gave only poor yields of unexpected products.[46] Pyrogallol under like conditions yields di-pyrogallylhydroquinone,[47]

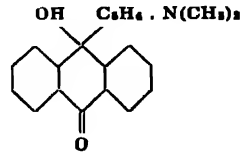


The reaction of anthraquinone with dimethylaniline in the presence of aluminum chloride results in formation of tetramethyldiaminodiphenylanthrone,

[45] P. R. Shildneck and R. Adams, *J. Am. Chem. Soc.*, 53, 352-353 (1931).
[46] R. Pummerer, M. Dally, and S. Remsinger, *Ber.*, 66, 792-796 (1933).
[47] R. Pummerer and G. Huppman, *Ber.*, 60, 1442-1451 (1927).

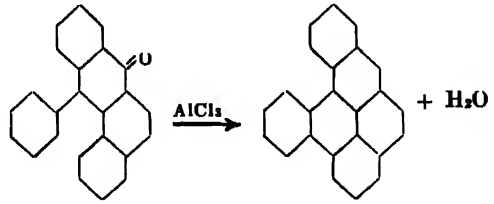


(m.p. 276-278°), together with dimethylaminophenyloxanthrol [48]:



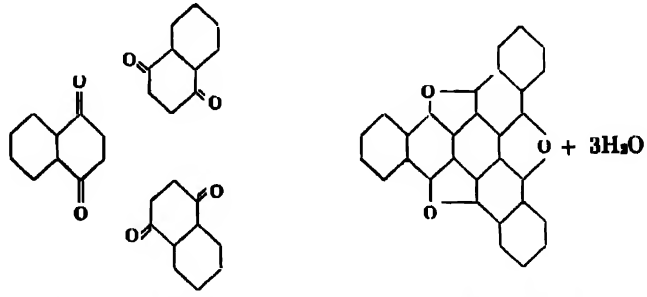
Hydrogenation Phenomena in Cyclization

When phenyl-1-naphthylphthalide is heated with 4 parts of aluminum chloride in absence of a solvent, at 130-165°, conversion to 1,2,3,4-dibenzopyrene occurs.[49]



A similar dehydrogenation and reduction was shown in the conversion of *meso*-diphenyldihydroxydihydro-1,2-benzanthracene to 5-phenyl-1,2,3,4-dibenzopyrene.

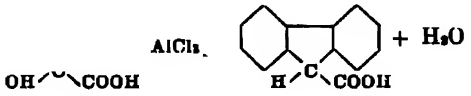
An interesting case of autocondensation is that of α-naphthoquinone, which upon heating for one-half hour at 50-60° with 0.5 its weight of aluminum chloride in nitrobenzene is converted into trinaphthobenzene trioxide in 60-65 per cent of theoretical yields.[50]



[48] R. Padowa, *Ann. chim. phys. (8)*, 19, 353-440 (1910); *C. Z.*, 1910 I, 1723.
[49] E. Clar, *Ber.*, 63, 112-120 (1930); *Brit. Chem. Abs.-A*, 334 (1930).
[50] C. Marschalk, *Bull. soc. chim. (5)*, 5, 304-306 (1938); *C. A.*, 32, 4751.

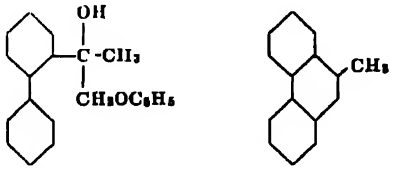
Reaction occurs with elimination of 3 molecules of H_2O, the hydrogen being supplied through dehydrogenation occurring at the 2,3-positions of the naphthoquinone.

Ring closure of benzilic acid occurs upon treatment with aluminum chloride:



There is thus secured 9-10 g of fluorene-9-carboxylic acid from 20 g of benzilic acid and 40 g of aluminum chloride suspended in 350 cc of benzene. The diluent may be replaced by carbon disulfide, but anhydrous ferric chloride and phosphorus pentoxide cannot be used instead of aluminum chloride.[51]

Cyclization of 1-methyl-1-(2-xenyl)-2-phenoxyethanol to 9-methylphenanthrene is effected in 10 per cent yield when the carbinol dissolved in carbon disulfide is treated with aluminum chloride and allowed to stand over night.[52]



Hydrogenation Phenomena in Friedel-Crafts Reactions

Reduction has been observed [53] in attempted reaction of 1,1-diaryl-2-acylethylenes with benzene and aluminum chloride. Instead of condensation, only hydrogenation to the corresponding saturated diaryl ketones occurred:

$$(Ar)_2C : CHCOR \xrightarrow[AlCl_3]{C_6H_6} (Ar)_2CHCH_2COR$$

Although it was found that the reaction involved also replacement of the aryl group, the origin of the hydrogen was unknown, for in other studies * dealing with the reversibility of the Friedel-Crafts reaction, hydrogenation had not been observed in replacement reactions involving addition to an olefinic linkage which is conjugated to a carbonyl group.

Hydrogenation phenomena in the Friedel-Crafts reaction has been noted by Nenitzescu and Isacescu [54] in the reaction of allyl chloride with

[51] D. Vorländer and A. Pritzsche, *Ber.*, **46**, 1793-1796 (1913).
[52] C. K. Bradsher and R. W. H. Tess, *J. Am. Chem. Soc.*, **61**, 2184-2185 (1939).
[53] L. L. Alexander, A. L. Jacoby, and R. C. Fuson, *J. Am. Chem. Soc.*, **57**, 2208-2209 (1935).
* See page 483.
[54] C. D. Nenitzescu and D. A. Isacescu, *Ber.*, **66**, 1100-1103 (1933); *Brit. Chem. Abs.*-A, 941 (1933)

benzene. The formation of an anthracene derivative in the condensation, with evolution of hydrogen, results in an anomalous course.*

Aluminum Chloride as a Hydrogenating Catalyst

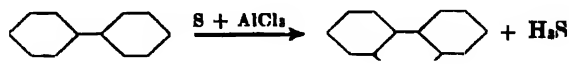
Since aluminum chloride is instrumental in condensing hydrocarbons with evolution of hydrogen, it has been suggested for use as catalyst in destructive hydrogenation of polycyclic aromatics.[55] Its usefulness for this purpose arises from its activity as a cleavage catalyst and as a dehydrogenating-condensation catalyst. It not only cracks the hydrocarbons into unsaturated compounds which are hydrogen-acceptors, but it also induces the production of hydrogen by promoting dehydrogenating condensations. When anhydrous aluminum chloride is used as catalyzer the hydrogenation can take place even without the external action of compressed hydrogen.[56]

Naphthalene with hydrogen under pressure at 500° is only partially hydrogenated. The use of aluminum chloride lowers the hydrogenation threshold temperature to 450° and increases the yield of liquid products and the content of these products in aromatic hydrocarbons, hydronaphthalenes, and hydroanthracenes.[57] The hydrogenation of petroleum fractions is effectively brought about by treatment with aluminum chloride-hydrocarbon complex and hydrogen,[58] or by heating with an activated aluminum chloride.[59]

Dehydrogenating Condensations with Sulfur and Sulfur Compounds

The reaction of sulfur with benzene in the presence of aluminum chloride at 75-80° was noted by Friedel and Crafts [60] to result in formation of diphenyl sulfide, thianthrene, and phenyl mercaptan. Later investigators [61] have confirmed the formation of diphenyl sulfide and thianthrene. The ratio of these products obtained was found to be a function of the aluminum chloride concentration, an increase in the catalyst favoring diphenyl sulfide formation.

Biphenyl reacts with sulfur in the presence of aluminum chloride to give dibenzothiophene:



* See page 121.

[55] S. B. Ansimov and V. F. Polosov, *J. Gen. Chem. U. S. S. R.*, 6, 1847-54 (1936). *C. A.*, 31, 4309. S. B. Ansimov, *Novosti Tekniki*, 5, No. 45, 17-18 (1936), *C. A.*, 31, 2401. A. Kling and D. Florentin, *Compt. rend.*, 182, 526-527 (1926), *C. A.*, 20, 1791; *ibid.*, 184, 822-824 (1927), *C. A.*, 21, 2470; *ibid.*, 193, 1198-1199 (1931), *Brit. Chem. Abs.-A*, 152 (1932). H. Winter and G. Free, *Brennstoff Chem.*, 12, 451-453 (1931), *C. A.*, 26, 1276. F. Fischer, *Ber.*, 49, 253-259 (1916), *C. A.*, 10, 1039.

[56] N. A. Orlov, *J. Russ. Phys.-Chem. Soc.*, Chem. Part 60, No. 9, 1447-1458 (1928); *Ber.*, 62, 710-719 (1929), *C. A.*, 23, 2174.

[57] A. Kling and D. Florentin, *loc. cit.*

[58] U. S. P. 1,954,481 (1934) to W. M. Stratford (to Texas Co.); *C. A.*, 28, 3886.

[59] E. Galle, *Petr. Z.*, 30, No. 8, 1-8 (1934); *C. A.*, 28, 3880.

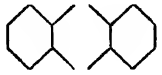
[60] C. Friedel and J. M. Crafts, *Compt. rend.*, 86, 884-887 (1878); *J. Chem. Soc. Abs.*, 670 (1878).

[61] J. Boeseken, *Rec. trav. chim.*, 24, 209-222 (1905). G. Dougherty and P. O. Hammond, *J. Am. Chem. Soc.*, 57, 117-118 (1935).

An I. G. Farbenindustrie patent [62] cites the production of an 80 per cent yield of dibenzothiophene by melting together 308 g of biphenyl with 128 g of sulfur, adding 15 g of aluminum chloride, and heating for fifteen minutes at 110°, for two hours at 110-115°, and finally for eight to ten hours at 230-240°. Following substantially the same procedure, Gilman and Jacoby [63] secured a 65-70 per cent yield.

The preparation of therapeutic compounds, useful for the treatment of scabies, is claimed by condensing toluene or xylene with sulfur and aluminum chloride by heating until hydrogen sulfide and hydrogen chloride evolution has ceased.[64]

The "Ferrario reaction" [65] is the condensation of diphenyl ether with sulfur in the presence of aluminum chloride to give an 87 per cent yield of phenoxthine,



This reaction has been extended to include 1,2, or 3 methyl- and 1,2, or 3-chlorodiphenyl ethers, with a somewhat lower yield of the corresponding phenoxthine derivative.[66] 4,4'-Dimethyldiphenyl ether yields 3,6-dimethylphenoxthine, but in the reaction of 4,4'-diacetyldiphenyl ether condensation was accompanied by reduction with formation of 3,6-diethylphenoxthine.[67] Diarylthioxines, such as phenoxthine, are claimed to be effective insecticides.[68]

Thiodiphenylamine and its derivatives can be prepared with yields up to 93 per cent by reacting diphenylamine with sulfur and aluminum chloride.[69] Thio-β-dinaphthylamine and thio-p-tolyl-β-naphthylamine and similar products may be prepared in an analogous manner.[70]

The improvement of lubricating oils or greases is said to be accomplished by the addition of compounds formed by the action of sulfur or organic sulfur compounds on olefins, oils, fats, or other high molecular weight materials in the presence of aluminum chloride.[71]

Oily substances obtained by the action of sulfur on toluene, xylene, etc. in presence of aluminum chloride have been claimed as effective additives to coatings made from chlorinated rubber.[72]

[62] German P. 579,917 (1933) to E. Tschunkur and E. Himmer (to I. G.); *C. A.*, **28**, 2053, *C. Z.*, 1933 II, 2457.
[63] H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108-119 (1938).
[64] German P. 365,189 (1922), Swiss P. 99,238 (1921), U. S. P. 1,426,430, and U. S. P. 1,427,182 (1922) to H. Weyland, H. Hahl, and R. Berendes (to Farb. Fabrik. Bayer and Co.); *C. A.*, **16**, 3732, *C. Z.*, 1923 II, 600.
[65] E. Ferrario, *Bull. soc. chim. (4)*, **9**, 536-537 (1911), *C. A.*, **5**, 3333; German P. 234,743 to F. Ackermann. C. M. Suter, J. P. McKenzie, and C. E. Maxwell, *J. Am. Chem. Soc.*, **58**, 717-720 (1936). C. M. Suter and C. E. Maxwell, *Org. Syntheses*, **18**, 64-65 (1938). M. Tomita, *J. Pharm. Soc. Japan*, **58**, 510-517 (1938); *C. A.*, **32**, 7467.
[66] C. M. Suter and F. O. Green, *J. Am. Chem. Soc.*, **59**, 2578-2580 (1937).
[67] M. Tomita, *J. Pharm. Soc. Japan*, **58**, 510-517 (1938); *C. A.*, **32**, 7467.
[68] U. S. P. 2,049,725 (1936) to L. E. Smith (to the free use of the public of the U. S. A.), *C. A.*, **30**, 6568.
[69] German P. 222,879 (1909) to F. Ackermann; *C. A.*, **4**, 2853 (1910).
[70] German P. 234,345 (1910) to F. Ackermann; *J. Chem. Soc. Abs. (I)*, 728 (1910).
[71] Brit. P. 435,548 (1935) to I. G.; *C. A.*, **30**, 1555.
[72] Brit. P. 429,764 (1933) to I. G.; *Brit. Chem. Abs.*-B, 755 (1935).

A 50 per cent yield of thianthrene may be secured by adding 36 g of aluminum chloride to 24 g of phenyl disulfide in 1 liter of petroleum ether during one hour and then boiling the solution for several hours. A small amount of thiophenol is secured as by-product. Under like conditions, *o*- and *p*-thiocresol yield dicresylsulfides, but no methylthianthrene. With *m*-thiocresol there is no reaction.[73]

The addition of an excess of aluminum chloride to phenyl mercaptan, dissolved in large excess of light petroleum, results in the formation of diphenyl sulfide and thianthrene. Hydrogen sulfide is evolved, together with a small quantity of hydrogen chloride.[74]

The effect of aluminum chloride on several sulfur compounds in benzene suspension at ordinary temperature has been investigated.[75] The following results were secured:

Initial Compound	Product
n-Primary amyl sulfide	little or no change
n-Primary amyl mercaptan	little or no change
Ethyl mercaptan	little or no change
Benzyl mercaptan	diphenylmethane
Benzyl sulfide	<2 moles $AlCl_3$—tribenzylsulfonium chloride >2 moles $AlCl_3$—diphenylmethane
s-Trithiane	<2 moles $AlCl_3$—sulfonium salt, and S >2 moles $AlCl_3$—diphenylmethane and benzyl sulfide

[73] J. J. B. Deuss, *Rec. trav. chim.*, **28**, 136-141 (1909); *C. A.*, **3**, 1747.
[74] J. J. Deuss, *Rec. trav. chim.*, **27**, 145-148 (1908).
[75] S. W. Lee and G. Dougherty, *J. Org. Chem.*, **4**, 48-53 (1939).

Chapter 14

Miscellaneous Condensations

The use of the anhydrides of aliphatic monocarboxylic acids to prepare alkyl aryl ketones gives products which are purer than those obtained from the corresponding acyl halides. This type of reaction is discussed in this chapter, and the products from various reactants are indicated. The reaction of similar aromatic acid anhydrides is also discussed, although this field has not been studied very extensively.

It is shown in a subsequent chapter * that aluminum chloride promotes the hydrolysis of organic esters. When such a cleavage of an ester occurs in the presence of an aromatic hydrocarbon it is evident that both alkylation and acylation are possible. Actually both reactions will occur, thus, the condensation of ethyl acetate with benzene in the presence of aluminum chloride produces both ethylbenzene and ethylacetophenone, the ratio of these products depending upon the reaction conditions.

As might be expected from the ease of alkylation with organic chlorides, alkylation is also possible with organic esters of other inorganic acids such as carbonic, chlorocarbonic, sulfonic, sulfuric, boric, silicic, and phosphoric acids. Reactions of this type are reviewed here.

Other condensations in the presence of aluminum chloride which have not been studied very extensively are also considered here. These include the preparation of ketones by the reaction of aliphatic or aromatic carboxylic acids with aromatic hydrocarbons, the alkylation of aromatic hydrocarbons with aliphatic ethers, cross-esterification between various organic compounds, and the nitration of benzenoid derivatives by the oxides of nitrogen.

Anhydrides of Mono-carboxylic Acids

Aliphatic Acid Anhydrides

Alkyl aryl ketones may be prepared by condensation of either acyl halides or acid anhydrides with aromatic hydrocarbons in the presence of aluminum chloride. Recently it has been shown that purer products are obtained with the anhydrides,[1] and that when yields are computed on total acyl content of the anhydride, they are of the same order as those obtained with acyl halides.

That condensation of aliphatic monocarboxylic anhydrides with aromatic hydrocarbons in the presence of aluminum chloride leads to pro-

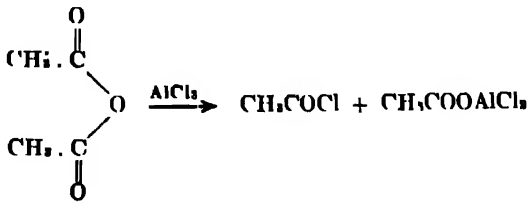
* See page 733.

[1] C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, 46, 1889-1896 (1924). P. H. Groggins and R. H. Nagel, *Ind. Eng. Chem.*, 26, 1313-1316 (1934).

duction of ketones has long been known. Friedel and Crafts [2] reported such condensation of benzene with acetic anhydride. Early investigators, using molecular equivalent, or less, of the catalyst obtained poor results. Michaelis, for example, notes that *p*-methylacetophenone may be obtained by gradual addition of 6 parts of aluminum chloride to a mixture of 10 parts of acetic anhydride and 40 parts of toluene, and subsequent heating.[3] Coinciding with the early announcements concerning the use of acetic anhydride for ketone synthesis came theories for the possible mechanisms involved. Adrianovsky [4] noted that aluminum chloride converts acetic anhydride into acetyl chloride. Gustavson [5] assumed a dual role for the catalyst, postulating a combination with benzene to form the complex $Al_2Cl_6.6C_6H_6$, and at the same time a conversion of the acid anhydride into chlorine compounds which later react on the $Al_2Cl_6.6C_6H_6$, with evolution of hydrogen chloride.

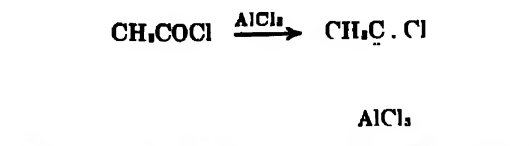
Until 1924, acid anhydrides were generally considered to be far less efficient than acyl halides for Friedel-Crafts ketone synthesis. New interest in the reaction was aroused by Noller and Adams,[1] who found that aliphatic acid anhydrides may very conveniently be used in place of acid chlorides in the Friedel-Crafts reaction if slightly over two moles of aluminum chloride are used for each mole of acid anhydride that is allowed to react.

Groggins and his co-workers [6] have shown that with two moles of aluminum chloride the maximum yield of ketone obtainable is 50 per cent when based on the availability of two acyl groups, and 100 per cent when based on the availability of only one acyl group. The first mole of catalyst effects cleavage of the anhydride:



$$CH_3.CO.O.CO.CH_3 \xrightarrow{AlCl_3} CH_3COCl + CH_3COOAlCl_2$$

The second mole produces an active complex with the acyl halide:



$$CH_3COCl \xrightarrow{AlCl_3} CH_3C(=O)Cl \cdot AlCl_3$$

[2] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 14, 455 (1888); *Compt. rend.*, 86, 1368 (1878).
[3] A. Michaelis, *Ber.*, 15, 185-186 (1882); *J. Chem. Soc. Abs.*, 870 (1882).
[4] A. Adrianovsky, *J. Russ. Phys.-Chem. Soc.*, 11, 116 (1879)
[5] G. Gustavson, *Ber.*, 12, 858 (1879); *J. Chem. Soc. Abs.*, 785 (1879).
[6] P. H. Groggins and R. H. Nagel, *loc. cit.*; P. H. Groggins, R. H. Nagel, and A. J. Stirton, *Ind.*, 26, 1317-1318 (1934).

However, if a third mole of aluminum chloride is used, the aluminum chloride salt of acetic acid which was primarily formed is also rendered active, probably according to the reaction:

$$CH_3COOAlCl_2 + AlCl_3 \qquad CH_3C.Cl + AlOCl$$

$$AlCl_3$$

This mechanism was confirmed by a long series of runs in which 5 moles of benzene and 1 mole of acetic anhydride were reacted at 90° with varying quantities of aluminum chloride. Data from some of these runs are reproduced, the percentage yields shown being based on the availability of both acetyl groups of the anhydride:

$AlCl_3$ moles	Time (hours)	Yield of Acetophenone (grams)	(%)	m.p. (°C)
1.1	5.5	28	12	18.2
2.3	5.5	124–128	52–53	18.7
3.3	5.5	182	76	18.8
3.3	11.0	193–200	80–83	18.6

The influence of catalyst amount on the yield of 4-methylacetophenone was shown to have a similar effect in the reaction of toluene with acetic anhydride. An 83 per cent yield, based on both acetyl groups, of 4-chloroacetophenone was obtained from 2 moles of the anhydride, 6.6 moles of the aluminum chloride, and 8 moles of chlorobenzene heated for eight hours at 30-105° and then at 105° for ten hours.

Experiments conducted in the presence of iron or aluminum showed that they caused no important variation in yield, and the feasibility of employing suitably designed vertical iron reactors for carrying out these reactions was suggested.

Since these investigations, optimum conditions for preparation of aryl alkyl ketones by Friedel-Crafts reaction of aliphatic monocarboxylic acid anhydrides and aromatic hydrocarbons have been the subject of a number of patents. The use of at least two [7] or three [8] molecular proportions of aluminum chloride has been claimed. Advantage is indicated in conducting the reaction by first treating the anhydride with aluminum chloride at 30-100°, removing the volatile acyl halide, and then reacting the residue with an aromatic compound at 100-130° in the presence of aluminum chloride.[9] The preparation of acetophenone from acetic anhydride and benzene, or of *p*-methylacetophenone from acetic anhydride and toluene may be promoted by adding halogen carriers such as metallic iron, aluminum, or zinc.[10] In the production of 4-chloroacetophenone,

[7] U. S. P. 1,906,797 (1934) to P. H. Groggins and R. H. Nagel (to the U. S. Secretary of Agriculture); *C. A.*, **28**, 5469.
[8] U. S. P. 1,991,743 (1935) to P. H. Groggins (to the U. S. Secretary of Agriculture); *C. A.*, **29**, 2175.
[9] U. S. P. 1,997,213 (1935) to P. H. Groggins and R. H. Nagel (to the U. S. Secretary of Agriculture); *C. A.*, **29**, 3033.
[10] U. S. P. 1,999,538 (1935) to P. H. Groggins and R. H. Nagel (to the U. S. Secretary of Agriculture); *C. A.*, **29**, 4027; *cf.* P. H. Groggins and R. H. Nagel, *Ind. Eng. Chem.*, **26**, 1313-1318 (1934).

acetic anhydride and chlorobenzene are mixed with anhydrous aluminum chloride at about 100° in a crystallizing pan until the conversion of the reactants to the anhydrous aluminum chloride addition compound is complete, and the material may then be discharged as a granulous mass.[11] A modified process comprises dropping the anhydride into benzene in the presence of 3 molecular equivalents of aluminum chloride.[12]

A list of other preparations effected with anhydrides of aliphatic monocarboxylic acids and aromatic hydrocarbons or phenol ethers in the presence of aluminum chloride follows. Since there is some doubt concerning the basis on which yields as reported in the original papers have been calculated, percentage yields are not noted here.

Aromatic Reactant	Anhydride	Product	Ref.
Benzene	acetic	acetophenone	1, 2
Toluene	acetic	*p*-methylacetophenone	1, 2
1,3,5-Trimethylbenzene	acetic	2,4,6-trimethylacetophenone	1
1,3,5-Triethylbenzene	acetic	2,4,6-triethylacetophenone	3
Bromobenzene	acetic	*p*-bromoacetophenone	1, 2
Chlorobenzene	acetic	*p*-chloroacetophenone	1, 2
Biphenyl	acetic	4-acetylbiphenyl	4
m-Diphenylbenzene	acetic	*p*-acetyl-*m*-diphenylbenzene	5
Anisole	acetic	*p*-methoxyacetophenone	1, 2
Resorcinol dimethyl ether	acetic	2,4-dimethoxyacetophenone	1
o-Cresyl methyl ether	acetic	3-methyl-4-methoxyacetophenone	1
m-Cresyl methyl ether	acetic	2-methyl-4-methoxyacetophenone	1
p-Cresyl methyl ether	acetic	5-methyl-2-methoxyacetophenone	1
β-Naphthyl methyl ether	acetic	2-methoxy-1-acetonaphthone	1
Toluene	chloroacetic	*p*-methyl-ω-chloroacetophenone	1
Toluene	propionic	*p*-methylpropiophenone	1
Anisole	propionic	*p*-methoxypropiophenone	1
p-Cresyl methyl ether	propionic	5-methyl-2-methoxypropiophenone	1
Bromomesitylene	propionic	bromopropiomesitylene	6
Toluene	butyric	*p*-methylbutyrophenone	1
p-Cresyl methyl ether	butyric	5-methyl-2-methoxybutyrophenone	1
Toluene	valeric	*p*-methoxyvalerophenone	1
o-Cresyl methyl ether	valeric	3-methyl-4-methoxyvalerophenone	1

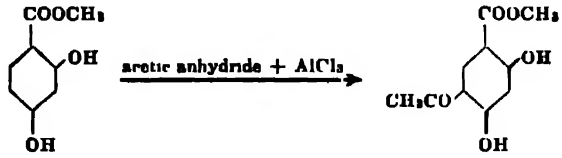
References

1. C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, 46, 1889-1895 (1924).
2. R. Adams and C. R. Noller, *Org. Syntheses*, V, 17-19 (1925).
3. R. C. Fuson and J. Corse, *J. Am. Chem. Soc.*, 60, 2063-2066 (1938); *C. A.*, 32, 8399.
4. N. L. Drake and J. Bronitsky, *J. Am. Chem. Soc.*, 52, 3715-3720 (1930).
5. H. Gaines Goodman, Jr., and A. Lowy, Paper presented at Am. Chem. Society meeting, Division of Organic Chemistry, Milwaukee, 1938.
6. R. Adams and M. W. Miller, *J. Am. Chem. Soc.*, 62, 53-6 (1940).

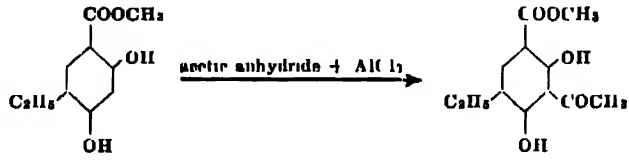
[11] U. S. P. 2,008,418 (1935) to P. H. Groggins (to the U. S. Secretary of Agriculture); *C. A.*, 29, 856

[12] German P. 646,702 (1937) to F. Unger (to I. G.); *C. A.*, 31, 6673.

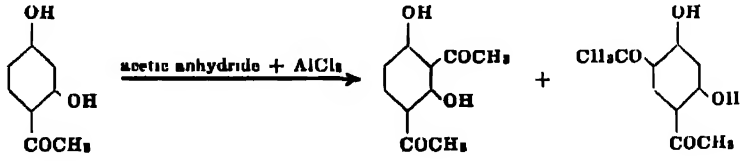
Aromatic *m*-dihydroxy esters or ketones may be acetylated by Friedel-Crafts reaction with acetic anhydride.[13] Although acetylation of methyl 2,4-dihydroxybenzoate cannot be effected by treatment with acetyl chloride, when the ester is treated with acetic anhydride and aluminum chloride in nitrobenzene, methyl 5-acetyl-2,4-dihydroxybenzoate is secured in good yield:



Like treatment of methyl 5-ethyl-2,4-dihydroxybenzoate gives methyl 2,4-dihydroxy-3-acetyl-5-ethylbenzoate:



Under similar conditions, 4-acetyl-1,3-dihydroxybenzene yields both 2,4- and 4,6-diacetyl-1,3-dihydroxybenzene:



Duvall and Mosettig[14] report rearrangement and acetylation of 4-acetoxyphenanthrene by Friedel-Crafts reaction with acetic anhydride A 61 per cent yield of 4-hydroxydiacetylphenanthrene was secured by mixing a solution of 9 g of 4-acetoxyphenanthrene and 3.96 ml of acetic anhydride in 45 ml of nitrobenzene with a solution of 5 64 g of aluminum chloride in 20 ml of nitrobenzene and allowing the mixture to stand for 48 hours.

The use of acetic anhydride in the presence of aluminum chloride for the acetylation of diphenylamine or of carbazole has been investigated by Boeseken.[15] According to Mitchell and Plant[16] the reaction with carbazole gives 3,6-diacetylcarbazole, m.p. 233°.

[13] R. D. Desai and M. Ekhlas, *Proc. Indian Acad. Sci.*, **8A**, 194-201 (1938). *Brit. Chem. Abs.*-A, II, 28 (1939); *C. Z.*, 1939 I, 2178.
[14] H. M. Duvall and E. Mosettig, *J. Am. Chem. Soc.*, **60**, 2409-2413 (1938).
[15] J. Boeseken, *Rec. trav. chim.*, **31**, 350-366 (1912).
[16] D. R. Mitchell and S. G. P. Plant, *J. Chem. Soc.*, 1295-1298 (1936); *C. A.*, **30**, 8211

Aromatic Monobasic Acid Anhydrides

Friedel-Crafts condensation with anhydrides of aromatic monobasic acids has not been extensively studied. Rubidge and Qua [17] have reported that benzophenone is obtained in poor yield by reaction of benzene with benzoic anhydride in the presence of aluminum chloride. Upon boiling for two hours a mixture consisting of 14.8 g of benzoic anhydride, 150 cc of benzene, and 20.5 g of aluminum chloride, they secured 6.3 g of benzophenone.

Like condensation with bromobenzoic anhydride, according to Cryer,[18] yields benzophenone together with some bromobenzophenone.

Zeavin and Fisher [19] reacted anhydrides of the following acids with benzene and aluminum chloride:

o-methoxybenzoic	*p*-nitrobenzoic
p-chlorobenzoic	3,5-dinitrobenzoic
p-bromobenzoic	β- and α-naphthoicbenzoic
m-nitrobenzoic	β- and α-naphthoicacetic

With all but the anhydrides of β- and α-naphthoicacetic acids and of *m*-nitrobenzoic acid, the only ketone formed was benzophenone. With *m*-nitrobenzoic anhydride a slight trace of *m*-nitrobenzophenone was secured together with benzophenone. α- and β-Naphthoicacetic acid anhydrides yielded acetophenone.

The reaction of the mixed anhydrides of benzoic and acetic acids with benzene and aluminum chloride gives almost a quantitative yield of benzophenone and very little acetophenone.[20]

Mitchell and Plant [16] report that the condensation of benzoic anhydride with carbazole in the presence of aluminum chloride in nitrobenzene yields 3,6-dibenzoylcarbazole.

Reaction of Saturated Esters with Aromatic Compounds

Carboxylic Acid Esters

The course of the reaction of esters with aromatic compounds in the presence of aluminum chloride varies with the individual ester used and with reaction conditions. Condensation proceeds with primary cleavage of the ester, and may be directed to result exclusively in alkylation or acylation of the aromatic component. Simultaneous alkylation and acylation has been reported. Although earlier investigators generally secured mixtures of alkylated and acylated products, more recent studies have revealed optimum conditions for the production of either ketones or alkyl derivatives. Cryer [21] reported acylation in the reaction of aspirin with benzene and aluminum chloride, a 70 per cent yield of acetophenone being

[17] C. R. Rubidge and N. C. Qua, *J. Am. Chem. Soc.*, 36, 732-737 (1914).
[18] J. Cryer, *Proc. Trans. Roy. Soc. Can. (3)*, 18, Sect. III, 119-120 (1924); *C. Z.*, 1925 I, 1402.
[19] J. M. Zeavin and A. M. Fisher, *J. Am. Chem. Soc.*, 54, 3738-3742 (1932); *C. A.*, 26, 5292.
[20] J. Cryer, *Trans. Roy. Soc. Canada (3)*, 19, Sect. III, 29 (1925); *Brit. Chem. Abs.*-A, 294 (1926).
[21] J. Cryer, *Trans. Royal Soc. Can., Sec. III (3)*, 19, 29 (1925); *C. A.*, 20, 408.

secured. Kaschtanow [22] found that a mixture of alkylated and acylated products was secured upon reaction of esters with benzene and aluminum chloride. The following condensations are reported:

Ester	Products
Ethyl acetate	ethylbenzene ethylacetophenone
Isoamyl acetate	*p*-diisoamylbenzene acetophenone
Ethyl valerate	ethylvalerophenone ethylbenzene
Isoamyl benzoate	diamylbenzene Product, b.p. 295-300°, which gave terephthalic acid upon oxidation
Benzyl benzoate	diphenylmethane *m*- and *p*-dibenzylbenzene

Ketonic products were likewise secured by Guyot [23] in the reaction of oxalic acid esters with *tert*-aromatic amines in the presence of a small amount of aluminum chloride at low temperatures:

$$R.COO.COOR + C_6H_5.NR'_2 \qquad ROH + R'_2N.C_6H_4.CO.COOR$$

With a higher ratio of catalyst at increased temperature, tetraalkyldiaminophenylglycolic acid esters were secured:

$$R.OOC.COOR + 2C_6H_5.NR'_2 \qquad ROH + (R'_2N.C_6H_4)_2COH.COOR$$

At still higher temperatures and a great excess of aluminum chloride the course of the reaction is directed toward formation of hexaalkyltriaminotriphenylacetic acid esters:

$$R.OOC.COOR + 3C_6H_5.NR'_2 \qquad ROH + (R'_2N.C_6H_4)_3C.COOR + H_2O$$

p-Acyldiphenyl ethers, together with larger amounts of Fries rearrangement products, have been obtained [24] upon heating *o*- or *p*-tolyl acetate, *m*-tolyl butyrate, or *o*-tolyl benzoate with diphenyl ether in the presence of aluminum chloride.

According to Bowden [25] reaction of benzene with esters proceeds smoothly, with formation only of alkylation products under definite reaction conditions, these varying with the sensitivity of the following types of esters:

(a) Esters that are easily alkylated.
(b) Esters of easily decomposed acids.
(c) Esters of stable acids.

[22] L. I. Kaschtanow, *J. Gen. Chem. (U. S. S. R.)*, 2, 515-523 (1932), *Brit. Chem. Abs.-A*, 1240 (1932), *C. Z.*, 1933 I, 600.
[23] A. Guyot, *Compt. rend.*, 144, 1051-1053 (1907); *C. Z.*, 1907 II, 144.
[24] E. H. Cox, *J. Am. Chem. Soc.*, 52, 351-355 (1930). For a discussion of Fries rearrangement, see page 696 of this book.
[25] E. Bowden, *J. Am. Chem. Soc.*, 60, 645-647 (1938).

Procedure (a) was used with ethyl acetate, isopropyl acetate, and *n*-butyl oxalate. It comprised the addition of 40 g of aluminum chloride to 250 ml of benzene, subsequent introduction of 0.25 mole of ester (or 0.125 mole of dibasic ester), and boiling under reflux for 0.5 to 1 hour. Yields of correspondingly alkylated benzenes were 60 per cent with ethyl acetate, 68 per cent with isopropyl acetate, and 55 per cent with *n*-butyl oxalate.

Procedure (b) involved the addition of 30 g of aluminum chloride to 250 ml of benzene, addition during four to nine hours of 0.25 mole of ester, standing over night, and gradually, during four hours, heating the reaction mixture to 60°. *n*-Propyl formate and *n*-propyl sulfite thus gave 66 per cent yields of *n*-propylbenzene. The formation of *n*-propylbenzene in this case is noteworthy, since alkyl halides and most esters give branched alkyl-benzenes. Using Bowden's procedure for the preparation of *n*-propylbenzene from benzene and *n*-propyl formate, however, Nightingale and Carton [26] subsequently found that the reaction of *m*-xylene with *n*-propyl formate yields 1,3-dimethyl-5-isopropylbenzene.

In procedure (c), Bowden used the same proportion of reactants and catalyst as in procedure (a), but since the esters used with this method were those of stable acids, longer reaction time was permissible, and the yield of alkyl benzene obtained was correspondingly greater. The catalyst was added to the benzene, and the ester was added in one portion. When esters of short-chain acids were used, the reaction mixture was allowed to stand over night before heating. With increasing molecular weight of the acid, heating was begun immediately. The reaction flask was immersed in a water-bath and heated very slowly, and no increase in heat was allowed until evolution of hydrogen chloride had practically ceased. The longer the chain of the acid, the more slowly reaction proceeded. This method gave the indicated yields of alkylbenzene from the following esters:

Ester	% Yield of Alkylbenzene
n-Butyl formate	73
n-Butyl propionate	92
n-Butyl isobutyrate	73
n-Butyl valerate	85
n-Butyl 2-ethylvalerate	78
n-Butyl benzoate	80
n-Butyl stearate	40

It is of interest that whereas a 92 per cent yield of product was secured from butyl propionate when 40 g of aluminum chloride was used, with 30 g of the catalyst, all of the ester was recovered unchanged.

The condensation of several alkyl esters of acetic acid with benzene in presence of aluminum chloride has been studied by Berman and Lowy [27] who report the following reactions:

[26] D. Nightingale and B. Carton, *J. Am. Chem. Soc.*, 62, 280-283 (1940).
[27] N. Berman and J. Lowy, *J. Am. Chem. Soc.*, 60, 2596-2597 (1938).

-acetate used	Moles	Moles of $AlCl_3$	Temp. (°C)	Time (hours)	Product: -benzene	% Yield
Isopropyl-	.49	.538		1	isopropyl-	13.6
Isopropyl-	.49	.538	80	20	isopropyl-	10.2
Isopropyl-	.245	.538	20–25	23	isopropyl	57.8
sec-Butyl-	.431	.945	80	10	*sec*-butyl-	15 6
sec-Butyl-	.431	.472	80	20	*sec*-butyl-	53.7
sec-Butyl-	.431	.0428	80	10	*sec*-butyl-	none
Methylamyl-	.347	.765	80	10	isohexyl-	none
Methylamyl-	.347	.191	80	10	isohexyl-	none
Methylamyl-	.347	.383	80	10	isohexyl-	48 0
Methylamyl-	.174	.191	80	10	isohexyl-	60 4

In the experiment with methylamyl acetate, the presence of mercury was found to be necessary for reaction to occur. The 48 and 60.4 per cent yields of isohexylbenzene were both secured in the presence of mercury; the amount of mercury used when the yield was 48 per cent is not given; the 60.4 per cent yield was secured in the presence of 10 g of mercury.

In another study [28] 0.45 mole of alkyl ester was reacted with 2 moles of dry benzene in the presence of 0.67 mole of aluminum chloride by refluxing on a water-bath for 5 hours. The following products were obtained with the indicated esters:

Ethyl acetate: 44% ethylbenzene; 23% *p*-ethylacetophenone; some isomeric diethylbenzenes; and a product, m.p. 182-3°.
Propyl acetate: 31.7% propylbenzene and a propylacetophenone, semicarbazone, m.p. 187.3-8.5°.
Butyl acetate: 31.8% butylbenzene and 9.1% butylacetophenone, semicarbazone, m.p. 189.5-90.5°.
Ethyl formate: No ketone; 63.3% ethylbenzene, 12.5% diethylbenzene; in some cases also 1,3,5-triethylbenzene.

According to Norris and Sturgis [29] the type of condensation product obtained depends not only on the ratio of catalyst to ester used and on the reaction conditions, but also on the manner in which the individual ester is decomposed. In the case of ethyl acetate, the ethyl-oxygen bond is broken more readily than the acetyl-oxygen bond.

$$CH_3COOC_2H_5 \qquad CH_3CO/C_2H_5$$

Hence, alkylation, rather than acylation is favored. The phenyl-oxygen bond, on the other hand, is broken only with difficulty: reaction of phenyl acetate and benzene in presence of aluminum chloride, therefore, gives acetophenone, although the yield of the ketone is affected by the fact that since phenyl acetate undergoes a Fries rearrangement, hydroxyacetophenones are also produced. With *o*-nitrophenyl acetate, which does not undergo a Fries rearrangement, an 82 per cent yield of acetophenone was secured.

Due to the fact that reaction of esters with benzene in presence of aluminum chloride proceeds with primary decomposition of the ester,

[28] D. N. Kursanov and R. R. Zel'vin, *J. Gen. Chem. (U. S. S. R.)*, 9, 2173-8 (1939); *C. A.*, 34, 4002
[29] J. F. Norris and B. M. Sturgis, *J. Am. Chem. Soc.*, 61, 1413-1417 (1939).

with formation of either alkyl halide or acyl halide, the first mole of catalyst used serves only to bring about cleavage. If formation of an alkyl halide has occurred, a slight excess of catalyst is sufficient to bring about alkylation of the aromatic component present. Since Friedel-Crafts ketone synthesis with acyl halides requires the use of a molecular equivalent of aluminum chloride, an additional mole of the catalyst must be used for production of ketones, if cleavage has proceeded with formation of acyl halide.

Condensation of ethyl acetate with benzene, using 0.5 mole of ester, 3 moles of benzene, and 1.2 moles of aluminum chloride at room temperature yields diethylbenzenes and higher substitution products; no ketones are formed. However, when the reaction mixture is heated for 200 hours at 100°, allowed to stand over night at room temperature, and heated for twelve hours at 100°, the chief product is diethylacetophenone, together with small amounts of ethylbenzene and acetophenone.

The course of the reaction of phenyl acetate with benzene was shown to be definitely influenced by the amount of catalyst used. Using aluminum chloride, ester, and benzene in the molecular ratio 1:1:4, no acetophenone was formed. The product consisted predominantly of unchanged ester, together with lesser amounts of phenol, and *o*- and *p*-hydroxyacetophenone. When the amount of catalyst was doubled, the ratio of reactants being 2:1:4, no acetate was recovered, and 43 to 60 per cent yields of acetophenone, depending on reaction time and temperature, were obtained. When toluene was substituted for benzene, using the same ratio of reactants, an 82 per cent yield of methylacetophenones was obtained.

In a later study, Norris and Arthur [30] showed that in the reaction of methyl and ethyl formates with benzene and toluene in the presence of aluminum chloride, alkylation alone takes place at lower temperatures; at higher temperatures, the acetates yield derivatives of acetophenone. The ketones secured from methyl acetate and benzene were *p*-methylacetophenone and 2,4-dimethylacetophenone. From ethyl acetate and benzene, *p*-ethylacetophenone and an unidentified higher boiling ketone were obtained. The ketonic fraction from the reaction of toluene with methyl acetate consisted principally of 2,4-dimethylacetophenone.

The orientation of the alkyl groups, as ascertained above by Norris and Arthur, differs from that reported in a patent on the production of nuclear alkylated aralkyl ketones by the action of esters of aliphatic or fatty aromatic acids with a mono- or polyvalent aliphatic alcohol on aromatic compounds of the benzene series in the presence of aluminum chloride; it is the subject of an I. G. Farbenindustrie patent.[31] The use of 2 moles of aluminum chloride for each ester group is specified. In reactions with substituted aromatic hydrocarbons, for example with ethylbenzene, the entering alkyl group goes *para*- to the substituent present, and the acyl residue in the *o*-position. When the reaction is

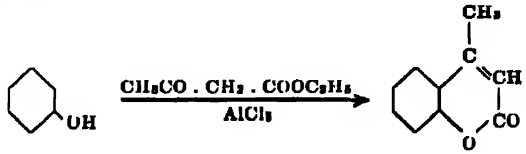
[30] J. F. Norris and P. Arthur, Jr., *J. Am. Chem. Soc.*, 62, 874-877 (1940).
[31] German P. 627,284 (1936) to I. G. Farbenindustrie; *C. Z.*, 1937 I, 3062; *C. A.*, 31, 703.

effected with benzene, the entering acyl- and alkyl- groups go *para*- to each other. Reaction of ethyl acetate with benzene is effected by adding, dropwise, 44 g of the ester to a mixture of 133 g of aluminum chloride in 39 g of benzene, allowing the reaction mixture to stand for 0.5 hour at the temperature which had been reached upon addition of the reactants, and subsequently heating it for two hours on a water-bath. After customary treatment, there is obtained a 55-65 per cent yield of *p*-ethylacetophenone. If larger amounts of aluminum chloride are used, acetophenone and 3,4-diethylacetophenone are also formed. Other reactions described include the following:

Hydrocarbon	Ester	Product
Benzene	methyl acetate	*p*-methylacetophenone
Benzene	ethyl butyrate	*p*-ethylbutyrophenone
Benzene	*n*-propyl butyrate	*p*-*n*-propylbutyrophenone
Benzene	isobutyl butyrate	*p*-*tert*-butylacetophenone
Benzene	ethyl phenylacetate	*p*-ethyldesoxybenzoin
Benzene	glycol diacetate	bis(*p*-acetylphenyl)-ethane
Benzene	cyclohexyl acetate	*p*-cyclohexylacetophenone
Ethylbenzene	ethyl acetate	*p*-ethylbenzophenone
		2,4,5-triethylacetophenone
		ethylbenzene
		poly-ethylbenzene

Reaction of esters of higher aliphatic acids with aromatic hydrocarbons or phenols in the presence of aluminum chloride for production of alkylated hydrocarbons or phenols has also been claimed.[32] An example cites the formation of a product (b.p. 230-265°/13 mm), consisting chiefly of cetylphenol, by gradually treating with 80 parts of aluminum chloride a mixture consisting of 200 parts of spermaceti and 50 parts of phenol at temperatures not exceeding 100°, holding the reaction mixture at 100° for about one hour, and heating it for two hours at 150-175°.

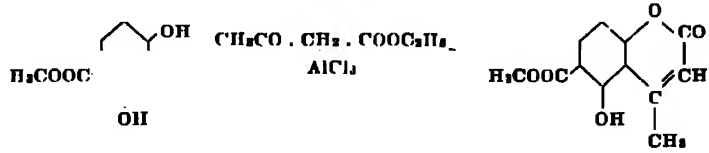
β-Ketonic Esters.—The condensation of β-ketonic esters with phenols in the presence of aluminum chloride proceeds with formation of coumarins. Ethyl acetoacetate with phenol gives a 30-40 per cent yield of 4-methylcoumarin [33]:



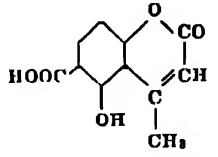
When reaction is effected in the presence of sulfuric acid instead of aluminum chloride the yield of the coumarin is only 3 per cent. Substituted phenols undergo like reaction with the ester and aluminum chloride. Also, *o*-hydroxyacetophenone and methyl *o*-hydroxybenzoate produce methyl-5-hydroxy-6-acetyl- and 5-hydroxy-6-carbomethoxycoumarin,

[32] U. S. P. 2,061,593 (1936) to J. D. Robinson (to National Aniline and Chemical Co.); *Brit. Chem. Abs.*-B, 1214 (1937).
[33] S. M. Sethna, N. M. and R. C. Shah, *Current Sci.*, 6, 93-94 (1937); *C. A.*, 32, 549; *Brit. Chem. Abs.*-A (II), 513 (1937).

respectively. Reaction of the ester and ketone is noteworthy, inasmuch as the carbonyl and carboxyl groups have an inhibiting effect on Friedel-Crafts condensations. The condensation was subsequently extended [34] to the preparation of hydroxycoumarins from acetoacetate and resorcinol derivatives. Methyl β-resorcylate gives a mixture of coumarins of which the predominate product is methyl 5-hydroxy-4-methylcoumarin-6-carboxylate:

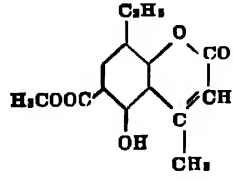


From 20 g of methyl β-resorcylate, 17 g of the keto-ester, and 32 g of aluminum chloride, there was secured 8 g of the above coumarin. Reaction was effected in nitrobenzene solution at 125-130° for one hour. The use of less or more than the 2 moles of catalyst was found to diminish the yield. Reaction with β-resorcylic acid analogously gave 5-hydroxy-4-methylcoumarin-6-carboxylic acid,



and resacetophenone gave 5-hydroxy-6-acetyl-4-methylcoumarin.

The same type of reaction occurs readily with 2,4-dihydroxy-5-ethylbenzoic acid or its methyl ester. Reaction of the ester occurred upon heating for one hour at 130-140° a mixture consisting of 11.5 g (1 mole) of the hydroxy ester, 10 g (1.3 mole) of ethylacetoacetate, and 16 g (2 moles) of aluminum chloride dissolved in 80 cc of nitrobenzene. There was secured 7.5 g of methyl 5-hydroxy-4-methyl-8-ethylcoumarin-6-carboxylate,



The corresponding acid was secured with 2,4-dihydroxy-5-ethylbenzoic acid.

Analogous reactions have been found to occur with ethyl acetoacetate and orcacetophenone, 2,4-dihydroxybenzophenone, 2-acetylresorcinol,

[34] S. M. Sethna, N. M. and R. C. Shah, *J. Chem. Soc.*, 228-232 (1935).

and phloracetophenone.[35] In a series of reactions in which various 4-acylresorcinols were condensed with ethyl acetoacetate, 5-hydroxy-6-acylcoumarin derivatives were obtained in all cases.[36]

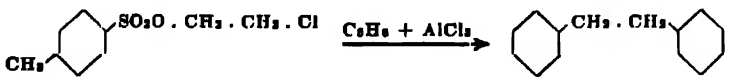
Reaction of alkylcyclohexanone-2-carboxylates or *trans*-β-decalone-3-carboxylate with di- or trihydric phenols in the presence of aluminum chloride leads to production of coumarins.[37] The cyclic β-ketonic esters were found to condense more readily than the corresponding open-chain esters.

Ethyl α-acetoglutarate likewise condenses with resorcinol in the presence of aluminum chloride to give a coumarin derivative.[38]

Esters of Inorganic and Sulfonic Acids

The use of esters of inorganic acids as alkylating agents in Friedel-Crafts reactions has been reported by various investigators. Friedel and Crafts[39] reported the alkylation of benzene by ethyl chlorocarbonate, and the reaction was subsequently noted by Rennie.[40] Kunckell and Ulex[41] found that esters of chlorocarbonic acid may be advantageously used in the preparation of alkylbenzenes; they described the preparation of toluene and xylene from methyl chlorocarbonate and benzene in the presence of aluminum chloride. Toluene was similarly reported to yield trimethylbenzene. The ethyl ester of chlorocarbonic acid yielded diethylbenzene and diethyltoluene from benzene and toluene, respectively. Isobutyl and amyl esters of chlorocarbonic acid were found to give better yields of alkylated products than the lower homologs.

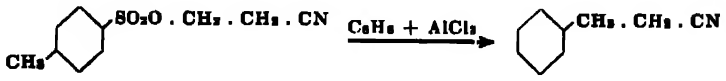
Subsequently, Clemo and Walton[42] found that aralkyl sulfonates could be used as alkylating agents in Friedel-Crafts condensations β-Chloroethyl *p*-toluenesulfonate with benzene and aluminum chloride yielded bibenzyl:



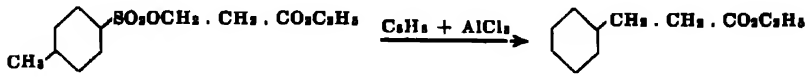
Here reaction had occurred with cleavage of the alkyl group of the sulfonate and addition of phenyl at the point of cleavage as well as by replacement of halogen. By heating, under reflux, a mixture consisting of 11.7 g of ester, 100 cc of benzene, and 20 g of aluminum chloride, there was obtained 7 g of bibenzyl. With the halogen-free ester, ethyl *p*-toluenesulfonate, addition takes place only at the point of cleavage, with production of ethylbenzene in 64 per cent yield. β-Cyanoethyl toluene-

[35] R. M. and R. C. Shah, *J. Chem. Soc.*, 1424-1428 (1938) R. D. Desai and M. Ekhlas, *Proc. Ind Acad. Sci.*, 8A, 567-577 (1938), *C. A.*, 33, 3356.
[36] C. V. Dellwala and N. M. Shah, *J. Chem. Soc.*, 1250-1253 (1939).
[37] N. A. Chowdhry and R. D. Desai, *Proc Ind. Acad. Sci.*, 8A, 12-19 (1938), *C. A.*, 32, 9066, *C. A.* 1939 II, 3683.
[38] N. M. Shah, *J. Univ. Bombay*, 8, Parts 3, 205-207 (1939); *Brit. Chem. Abs.-A*, 1940 II, 127
[39] C. Friedel and J. M. Crafts, *Compt. rend.*, 84, 1450 (1877).
[40] E. H. Rennie, *J. Chem. Soc.*, 41, 33 (1882).
[41] F. Kunckell and G. Ulex, *J. prakt. Chem. (2)*, 86, 518-530 (1912); *J. Chem. Soc. Abs.*, 104 (I) 29 (1913).
[42] G. R. Clemo and E. Walton, *J. Chem. Soc.*, 728-730 (1928), *C. A.*, 22, 1964.

p-sulfonate under similar treatment gives a 72 per cent yield of β-phenylpropionitrile:



β-Carbethoxyethyl toluene-*p*-sulfonate gives ethyl β-phenylpropionate in 74 per cent yield:



Alkylation has also been claimed to be effected by reaction of trialkyl or triaralkyl borates with aromatic compounds in the presence of aluminum chloride.[43] Triisobutyl borate and *m*-xylene react according to the equation:

$$3(CH_3)_2 . C_6H_4 + [(CH_3)_2CHCH_2]_3BO_3 \xrightarrow{AlCl_3}$$
$$3(CH_3)_2 . C_6H_2 . C(CH_3)_3 + 3HCl + AlBO_3$$

A 90 per cent yield of *tert*-butylxylene (b.p. 201-203°) is thus obtained. Other reactions which may be likewise effected comprise the condensation of triisobutyl borate with the indicated aromatic compounds:

Reactant	Product
Anisole	*p-tert*-butylanisole
Phenol	*p-tert*-butylphenol
Bromobenzene	*p*-bromo-*tert*-butylbenzene

When tribenzyl borate is reacted with benzene and aluminum chloride, the product is diphenylmethane.

Alkyl esters of sulfuric, orthosilicic, and carbonic acids have been found to be efficient alkylating agents.[44] Reaction proceeds according to the general schemes:

$$3(RO)_2SO_2 + 6C_6H_6 + 2AlCl_3 \longrightarrow 6C_6H_5R + 6HCl + Al_2(SO_4)_3$$
$$3(RO)_2CO + 6C_6H_6 + 2AlCl_3 \longrightarrow 6C_6H_5R + 6HCl + Al_2(CO_3)_3$$
$$3(RO)_4Si + 12C_6H_6 + 4AlCl_3 \longrightarrow 12C_6H_5R + 12HCl + Al_4(SiO_4)_3$$

The best yields of monoalkylated benzene obtained with the following esters are given:

Ester	% Yield of mono-alkyl benzene	Ester	% Yield of mono-alkyl benzene
Dimethyl sulfate	59.8	Dibutyl sulfate	43.6
Diethyl sulfate	71.4	Tetraethyl orthosilicate	53.3
Diisopropyl sulfate	44.2	Diethyl carbonate	56.4

Except in the case of the silicate, the optimum ratio of aluminum chloride to ester was 1.44:1. Higher ratio of catalyst resulted in more

[43] French P. 730,084 (1932), German P. 555,403 (1930) to A. Kaufmann, *C. A.*, **26**, 5101.
[44] H. L. Kane and A. Lowy, *J. Am. Chem. Soc.*, **58**, 2605-2608 (1936).

dialkylation. With the silicate the ratio of catalyst to ester was 2.88:1. The alkylation of naphthalene with diethyl sulfate was attempted, but the product was a hydrocarbon oil which could not be fractionated into separate ethylated derivatives.

According to Norris and Sturgis,[45] the condensation of diethyl carbonate with benzene in the presence of aluminum chloride yields 24.5 per cent ethylbenzene, 14 per cent *m*-diethylbenzene, and 32 per cent *sym*-triethylbenzene, based on the utilization of the two ethyl groups of the carbonate, if reaction is effected in the cold, or 53 per cent ethylbenzene and 16 per cent *sym*-triethylbenzene if heating is employed.

The use of trialkyl phosphates or of *tert*-butyl hypochlorite as alkylating agents in Friedel-Crafts synthesis has been investigated by Berman and Lowy.[46] Condensation occurs according to the scheme:

$$(RO)_3PO + 3C_6H_6 + AlCl_3 \longrightarrow 3RC_6H_5 + AlPO_4 + 3HCl$$
$$t\text{-}C_4H_9OCl + C_6H_6 + (AlCl_3) \longrightarrow t\text{-}C_4H_9C_6H_5 + HOCl$$

The reactions studied with benzene are summarized:

Ester	Moles	Moles of $AlCl_3$	Temp (°C)	Time (hours)	Product -benzene	% Yield
Triethyl phosphate	0.137	0.515	20–25	10	ethyl-	61.5
Triisopropyl phosphate	.112	.368	10–15	4	isopropyl-	52.1
Tributyl phosphate	.094	.353	20–25	2	*sec*-butyl-	71.5
t-Butyl hypochlorite	.277	.253	20–25	25	*t*-butyl	43.1

n-Propyl- and *n*-butyl sulfites have been used as alkylating agents. A 66 per cent yield of alkylated benzene was obtained when 30 g of aluminum chloride was added to 0.25 mole of *n*-propyl sulfite in 250 ml of benzene; the reaction mixture was allowed to stand over night, then heated for four hours, during which time the temperature was gradually raised to 60°. With *n*-butyl sulfite, 40 g of aluminum chloride was added in several portions to the quantity of ester and benzene used above, and the reaction mixture was immediately boiled under reflux for about an hour.[47]

n-Butyl chlorosulfonate has been investigated as an alkylating agent.[48] From a series of runs it was concluded that optimum conditions comprise maintenance of temperature at 0-5°, and the use of a 2:1 molar ratio of aluminum chloride and ester, and of about 9 moles of hydrocarbon.

Condensation of alkyl nitrates with aromatic hydrocarbons in the presence of aluminum chloride results not in alkylation but in nitration. In 1908, Boedtker[49] observed that condensation of benzene and ethyl nitrate with aluminum chloride yielded nitrobenzene, and that *p*-nitrotoluene was analogously obtained when toluene was used instead of ben-

[45] J. F. Norris and B. M. Sturgis, *J. Am. Chem. Soc.*, 61, 1413-1417 (1939).
[46] N. Berman and A. Lowy, *J. Am. Chem. Soc.*, 60, 2596-2597 (1938).
[47] E. Bowden, *J. Am. Chem. Soc.*, 60, 645-647 (1938).
[48] C. Barkenbus, R. L. Hopkins, and J. F. Allen, *J. Am. Chem. Soc.*, 61, 2452-2453 (1939).
[49] E. Boedtker, *Bull. soc. chim. (4)*, 3, 726-729 (1908); *C. Z.*, 1908 II, 403.

zene. Since the catalyst reacted very violently with ethyl nitrate itself, an excess of hydrocarbon was recommended for nitration with alkyl halides. The preparation of nitrosobenzene, but only in very small yield, was effected by reaction of amyl nitrite with benzene in presence of aluminum chloride.

Subsequently, the influence of varying ratios of aluminum chloride on yields of nitrobenzene from benzene and ethyl nitrate was studied.[50] The indicated amount of catalyst with equimolecular proportions of ethyl nitrate and benzene gave the following yields of nitrobenzene:

Moles of $AlCl_3$	% Yield of nitrobenzene
0.1	12
0.3	39.5
0.5	50.8
1.0	16.0

Nitration could also be affected by reaction of benzene with the material resulting from addition of aluminum chloride to ethyl nitrate.

Reaction of ethyl nitrate with naphthalene in the presence of aluminum chloride has been found to give 4-nitronaphthalene exclusively.[51]

Condensation of Carboxylic Acids with Aromatic Hydrocarbons

Carboxylic acids may be condensed with aromatic compounds to form alkyl aryl and diaryl ketones.[52] Reaction probably occurs through the course:

$$RCOOH + AlCl_3 \longrightarrow RC(=O)OAlCl_2 + HCl$$

$$RC(=O)OAlCl_2 + AlCl_3 \longrightarrow RC(=O)Cl + AlOCl$$

$$RC(=O)Cl + R' \longrightarrow R.C(=O).R' + HCl$$

(the carbonyl oxygen in each case bears a dotted bond to $AlCl_3$)

The condensation is therefore best effected in the presence of at least 2 moles of catalyst; and the use of 2.5 moles has been found advantageous. The following results are reported, using 5 moles of hydrocarbon and 1 mole of the indicated acid:

[50] B. V. Tronov and H. K. Sibgatullin, *J. Russ. Phys.-Chem. Soc.*, **62**, 2267-2272 (1930); *C. A.*, **25**, 3978.

[51] H. Wilstaedt and G. Sheiber, *Ber.*, **67**, 466-474 (1934); *C. A.*, **28**, 3069.

[52] P. H. Groggins, R. H. Nagel, and A. J. Stirton, *Ind. Eng. Chem.*, **26**, 1317-1318 (1934); U. S. P. 1,966,797 (1934) to P. H. Groggins and R. H. Nagel.

Acid	Hydrocarbon	Moles of $AlCl_3$	Temp. (°C)	Time (hours)	% Yield of Ketone
Acetic	benzene	2.5	86	10	67.0
Acetic	benzene	3.0	86	5.5	64.1
Acetic	toluene	2.0	106	7	61.2
Acetic	toluene	2.5	106	7	80.0
Benzoic	chlorobenzene	3.0	108	6	73.8

Similar condensations were effected with propionic acid and toluene, and with acetic acid and biphenyl, giving yields of ketones of the same order. It was found that formic acid could not be used as the carboxylic component, condensation leading to the formation of aldehydes.

The preparation of chlorobenzophenones by condensation of benzoic acid, 4-chlorobenzoic acid, 4-methylbenzoic acid, or terephthalic acid with chlorobenzenes was subsequently investigated.[53] Condensation occurred with formation of *o*- and *p*-isomeric benzophenones in practically quantitative yields. *p*-Substitution was favored:

Acid	Chlorobenzene	-benzophenone	% Yield
Benzoic	chlorobenzene	4-chloro	82.35
		2-chloro	11.9
		unseparated isomers	3.25
p-Toluic	chlorobenzene	4-chloro-4′-methyl	81.5
		2-chloro-4′-methyl	10.9
		unseparated isomers	3.6
Benzoic	1,2-dichlorobenzene	3,4-dichloro	79.5
		2,3-dichloro	11.0
		unseparated isomers	4.5
Terephthalic	1,2-dichlorobenzene	3,3″,4,4″-tetrachloro-4′-benzoyl	84
		other isomers	13

Norris and Klemka [54] have reacted 0.2 mole of benzoic acid with 0.44 mole of toluene by refluxing for 6 hours in presence of 0.4 mole of aluminum chloride. About a 40 per cent yield of *p*- and a 20 per cent yield of *o*-tolyl phenyl ketones was obtained. The reaction did not proceed so well when benzene was used instead of toluene, about 90 per cent of the benzoic acid being recovered.

Reaction of Ethers with Aromatic Hydrocarbons and Phenols

Diethyl ether has been reported by Jannasch and Bartels [55] to condense with benzene in the presence of aluminum chloride to give primarily hexaethylbenzene, together with some tetra- and pentaethylbenzene. Later, Jannasch and Rathjen [56] found that diethylphenol is obtained in excellent yield when 300 g of phenol and 300 g of ethyl ether are treated, with cooling, with 1200 g of aluminum chloride and then heated at 145° until reaction has ended. If the ratio of ether to phenol is increased, a more highly alkylated product is obtained. Thus, 100 g

[53] H. P. Newton and P. H. Groggins, *Ind. Eng. Chem.*, **27**, 1397-1399 (1935).
[54] J. F. Norris and A. J. Klemka, *J. Am. Chem. Soc.*, **62**, 1432-1435 (1940).
[55] P. Jannasch and A. Bartels, *Ber.*, **31**, 1716-1718 (1898).
[56] P. Jannasch and A. Rathjen, *Ber.*, **32**, 2201-2204 (1899).

of phenol with 180 g of ether and 550 g of aluminum chloride gives a good yield of tetraethylphenol.

Wedekind and Haussermann,[57] however, were unable to effect ethylation of benzene or phenol by reaction with diethyl ether in presence of aluminum chloride.

Recently, Norris and Sturgis [58] have found that the reaction may be regulated in such a way as to give either ethylbenzene or *sym*-triethylbenzene. By adding, during one hour, 1 mole of aluminum chloride to a mixture of 0.5 mole of ether in 3 moles of benzene, allowing the reaction mixture to stand over night, and subsequently heating for eight hours at 100-110°, a 36 per cent yield of ethylbenzene was secured. Reaction proceeded through intermediate formation of the molecular compound, $(C_2H_5)_2O.AlCl_3$.

Malson and Gardner [59] describe the condensation of diisopropyl ether and di-*n*-butyl ether with benzene by means of aluminum chloride. These investigators found that when the molal ratio of diisopropyl ether to Al_2Cl_6 exceeds 1:6, the yield of isopropylbenzene is greatly reduced. In order to prevent further reaction of the primarily formed mono-alkyl benzene, an apparatus was devised to remove the isopropylbenzene from the reaction zone upon its formation. The catalyst was placed in an extraction thimble held in a reaction tube which resembled a Soxhlet extractor in construction. The tube was left open at the bottom, and no syphon was used; it was attached to a 500-cc flask and provided with a reflux condenser. The ether and benzene were boiled in the flask at such a rate that the catalyst was continuously covered with liquid. Since the alkyl benzene formed is higher boiling, it was not circulated over the catalyst, and thus further reaction was prevented. This method could not be used with di-*n*-butyl ether because of its high boiling point; in this case the ether was added to the thimble by means of a dropping funnel. Monoalkyl benzenes in 20-48 per cent yields were obtained.

The condensation of ethyl benzyl ether with benzene and aluminum chloride has been reported by Kaschtanov [60] to give a mixture of ethylbenzene, diphenylmethane, and *m*- and *p*-dibenzylbenzene.

Cross-esterification of Phenol Esters

Cross-esterification of phenol esters of carboxylic acids is readily effected in presence of aluminum chloride.[61] Treatment of hydroquinone dibenzoate with isoamyl alcohol yields the phenol and isoamyl benzoate in 83.4 per cent of theoretical yield:

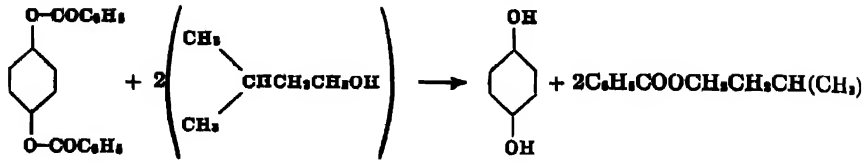
[57] E. Wedekind and J. Haussermann, *Ber.*, 34, 2081-2082 (1901).

[58] J. F. Norris and B. M. Sturgis, *J. Am. Chem. Soc.*, 61, 1413-1417 (1939).

[59] P. E. Malson and J. H. Gardner, "Condensation of Ethers with Benzene by Means of Aluminum Chloride." Paper presented to the Division of Organic Chemistry, American Chemical Society, Baltimore, 1939.

[60] L. I. Kaschtanov, *J. Gen. Chem. U. S. S. R.*, 2, 515-523 (1932); *Brit. Chem. Abs.*-A, 1240 (1932).

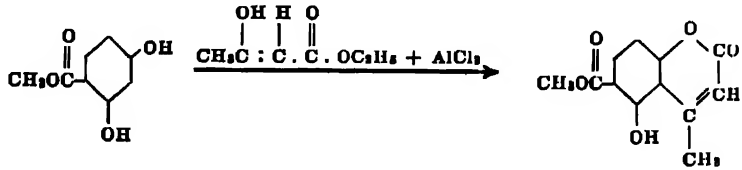
[61] G. A. Varvoglis, *Ber.*, 71, 2488-2492 (1938)



Cross-esterification may be effected with *o*- and *m*-dihydroxybenzene dibenzoates or their halogen substitution products in the same way. Higher-boiling alcohols are more reactive than the lower.

It has been shown by von Auwers and Mauss [62] that reciprocal esterification may occur during Fries rearrangements. Thus, a mixture of the acetate of 2-hydroxymesitylene with 3-chloro-*p*-tolyl benzoate gives free phenols, 3-chloro-2-hydroxy-5-methylacetophenone, the corresponding benzophenone, and the benzoate of 2-hydroxymesitylene.

Ethyl acetoacetate reacts smoothly, through the enol form, with methyl β-resorcylate in the presence of aluminum chloride with formation of methyl 5-hydroxy-4-methylcoumarin-6-carboxylate:

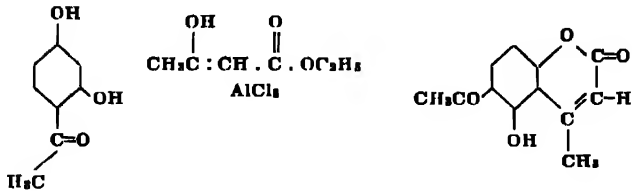


The reaction was effected with 1 mole of each ester in nitrobenzene in the presence of 2 moles of aluminum chloride at 125-130° for one hour. Condensation of β-resorcylic acid or of resacetophenone with ethyl acetoacetate proceeds similarly, yielding 5-hydroxy-4-methylcoumarin-6-carboxylic acid and 5-hydroxy-6-acetyl-4-methylcoumarin respectively.[63]

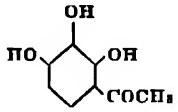
2,4-Dihydroxy-5-ethylbenzoic acid and its methyl ester yield 5-hydroxy-4-methyl-8-ethylcoumarin-6-carboxylic acid or the methyl ester, respectively.[64] In an investigation [65] of the reaction with di- and trihydroxyphenyl ketones, it was shown that orcacetophenone, 2,4-dihydroxybenzophenone, 2-acetylresorcinol, or phloroacetophenone may also be converted to the corresponding 5-hydroxycoumarins by the same procedure. It was suggested that the formation of coumarins from the resorcinol derivatives investigated depends upon the reactivity in the 2-position in the resorcinol nucleus; the chelation between the acyl and the *o*-hydroxyl groups fixes the double bonds in the nucleus, the condensation then taking place at the 3-position with subsequent ring closure to a 5-hydroxycoumarin. This type of addition is apparent in resacetophenone which condenses with acetoacetic ester by cross-esterification and

[62] K. von Auwers and W. Mauss, *Ann.*, 464, 293-311 (1928); *Brit. Chem. Abs.*-A, 1013 (1928)
[63] S. M. Sethna, N. M. and R. C. Shah, *J. Chem. Soc.*, 228-232 (1938).
[64] S. M. Sethna and R. C. Shah, *J. Chem. Soc.*, 1066-1069 (1938).
[65] N. M. and R. C. Shah, *J. Chem. Soc.*, 1424-1428 (1938).

displacement of the 2-hydrogen to yield 5-hydroxy-6-acetyl-4-methyl coumarin,



No such ring closure is possible with gallacetophenone,



because the 5-carbon, where the condensation might be expected to occur, is not reactive, since it is united by a single bond to a carbon atom bearing the hydroxyl group.

Nitration with Nitrogen Peroxide

Nitration of benzenoid compounds may be effected by treatment with nitrogen peroxide in the presence of aluminum chloride. According to Schaarschmidt,[66] reaction proceeds with intermediate formation of a complex of the three components, which upon hydrolysis yields the mono-nitrobenzenoid and nitrous acid. The nitrous acid decomposes into nitric acid and pure nitric oxide; the latter, after treatment with oxygen or air, is used for further charges. The most suitable molecular proportion of aluminum chloride, benzenoid compound, and nitrogen peroxide was found to be 0.66:3:1. A technical process has been worked out.[67]

It has been recently reported [68] that the nitration of benzene or chlorobenzene with nitrogen peroxide may be effected at 0° in the presence of aluminum chloride, but that only impure products are secured in attempted reactions with nitrobenzene, benzoyl chloride, or *p*-nitrotoluene.

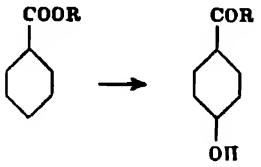
[66] A. Schaarschmidt, *Ber.*, 57, 2068-2072 (1924). A. Schaarschmidt, H. Balszerkiewicz, and J. Gante, *Ber.*, 58, 499-502 (1925).
[67] A. Schaarschmidt, *Z. angew. Chem.*, 39, 1457-1460 (1926); *C. A.*, 21, 3055.
[68] A. I. Titov, *J. Gen. Chem. (U. S. S. R.)*, 7, 591-594, 667-672 (1937); *Brit. Chem. Abs.*-A, 831 (1937).

Chapter 15

Aromatic Rearrangements and Migrations

Rearrangement of the substituting groups in aromatic compounds is frequently facilitated by the use of anhydrous aluminum chloride. Nuclear bound alkyl may migrate in either an intramolecular or an intermolecular manner. Acyl substituents may also rearrange to new positions on the aromatic nucleus. The subject of halogen migration has received considerable study, and it has been concluded that halogen substituents are set free as highly active nascent atoms, promoting a consequent wide range of possible reactions.

The rearrangement of phenolic esters to hydroxy aromatic ketones



is known as the Fries rearrangement. The mechanism of this reaction has been studied at some length with fairly general agreement that an intermolecular change is involved. There are several complicating factors in some reactions of this type which are discussed in this chapter and the results summarized.

Other rearrangements less widely studied include the formation of substituted phenols from alkyl phenyl ethers and the conversion of *sym*-acid chlorides of dicarboxylic acids into the lactone form.

Migration of Nuclear Alkyl Groups

The rearrangement of alkylated benzenes in the presence of aluminum chloride has been discussed in that section of this book which deals with the effect of aluminum chloride on aromatic hydrocarbons.* Recently, the effect of different classes of substituents on the change of position brought about by aluminum chloride has been investigated.[1] The chloro-substituent in toluene evidently does not hinder the migrating effect brought about by aluminum chloride; but under the conditions used to cause rearrangement of the chlorotoluenes, the isomeric nitrotoluenes and *p*-dimethylaminotoluene were not affected. Rearrangement of *p*-cresol was easily effected.

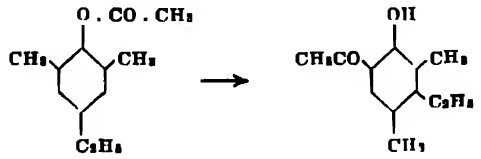
That the hydroxy group does not have an inhibiting effect on migration

* See page 712.

[1] J. F. Norris and H. S Turner, *J. Am Chem. Soc.*, 61, 2128-2131 (1939).

of alkyl groups had been previously demonstrated[2] in the transfer of alkyl groups from *p-tert*-butylphenol or *p-tert*-amylphenol to benzene upon heating a mixture of the phenol and benzene with aluminum chloride, yielding the respective alkylbenzenes.

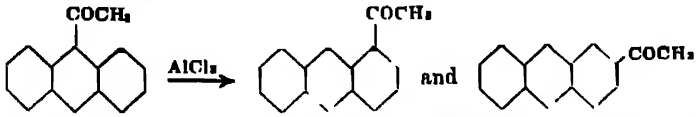
Migration of methyl groups is often apparent during Fries rearrangement. Wandering of the methyl group usually takes place when the acetyl group migrates to the *o*-position and there are present alkyl groups in the 2- and 5-positions.[3] An ethyl group is more easily affected than a methyl group. When ethyl groups are present in both *o*- and *p*-positions, the *o*-group is eliminated, the displaced group wandering into the *p*-position to that originally occupied.[4] That the case of displacement is not a function of the number of carbon atoms in the alkyl chain is shown by the fact that the ethyl group is more readily displaced than the propyl.[5] A methyl group, forced to migrate by an acid residue can itself displace an ethyl group[6]:



According to Mayer and his co-workers,[7] migration of a methyl group may occur during Scholl ring closure. Upon treatment of *o*-toluyl-α-naphthalene with aluminum chloride, the product is not the expected 5-methylbenzanthrone, but the 6-isomer. 2-Methyl-1-benzoylnaphthalene likewise gives 2-methylbenzanthrone instead of the 4-isomer upon ring closure. Baddar and Warren[8] report the synthesis of 2'-methyl-*meso*-benzanthrone from 3'-methyl-*meso*-benzanthrone by heating the 3'-isomer in an $AlCl_3$-NaCl melt for 2½ hours. On the other hand, 6-alkylbenzanthrones, *e.g.*, 6-propylbenzanthrone, are converted into benzanthrone when heated with aluminum chloride.[9]

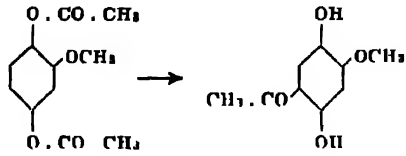
Migration of Nuclear-bound Acyl Groups

meso-Anthracyl alkyl ketones are converted into α- and β-anthracyl alkyl ketones by the action of aluminum chloride at a raised temperature or in high concentration[10]:



[2] R. A. Smith and C. J. Rodden, *J. Am. Chem. Soc.*, 59, 2353 (1937). R. A. Smith, *J. Am. Chem. Soc.*, 59, 899-900 (1937).
[3] K. v. Auwers, H. Bundesmann, and F. Wieners, *Ann.*, 447, 162-196 (1926).
[4] K. von Auwers and W. Mauss, *Ann.*, 460, 240-277 (1928).
[5] K. v. Auwers and E. Janssen, *Ann.*, 483, 44-65 (1930).
[6] K. v. Auwers and W. Mauss, *Ber.*, 61, 1495-1507 (1928); *C. A.*, 22, 4490.
[7] F. Mayer, E. Fleckenstein, and H. Günther, *Ber.*, 63, 1464-1472 (1930).
[8] F. G. Baddar and F. L. Warren, *J. Chem. Soc.*, 948-949 (1939).
[9] E. Ghigi, *Atti X Congr. Internaz. Chim.*, 1938, III, 178-183; *Brit. Chem. Abs.*-A II, 161 (1940).
[10] German P. 490,051 (1926) to A. Luttringhaus and F. Kacer, *C. A.*, 24, 4055; German P. 492,247 to I. G., *C. A.*, 24, 3472.

That the acyl group is susceptible to migration is shown by the fact that cleavage of acyl groups during Fries rearrangement of polyhydroxyphenols has been observed by Mauthner.[11] Thus methoxyhydroquinone diacetate, upon treatment with aluminum chloride in nitrobenzene solution, gives only a monoacylated product:



Migration of the acyl group has been noted during aluminum chloride hydrolysis of acylated naphthol ethers.[12] When the ethyl ether of 4-acetyl-1-naphthol is heated with aluminum chloride in carbon disulfide, there is formed not only 4-acetyl-1-naphthol, but also 2,4-diacetyl-1-naphthol. The aluminum chloride not only hydrolyzes the ether, but cracks off an acetyl group and reintroduces it, with formation of a diacylated product. Such a cleavage has also been noticed in the Fries rearrangement of α-naphthol esters, the rearranged product consisting not only of *o*- and *p*-hydroxy ketones but also of 2,4-diacyl derivatives of α-naphthol.[13]

That an acyl group attached to the oxygen atom of one phenol may enter the nucleus of another phenol molecule has been demonstrated by von Auwers and Mauss,[14] who found that when *p*-tolyl acetate is heated with 2-*m*-xylyl methyl ether and aluminum chloride, the product consists of xylenol, cresol, 2-hydroxy-5-methylacetophenone, and 4-hydroxy-3,5-dimethylacetophenone.

Alkylation by Transfer of Alkyl Radicals from Benzene Homologs

When alkylated aromatic hydrocarbons or their derivatives are heated with aluminum chloride, cleavage of alkyl groups may result.* When such cleavage is effected in the presence of another aromatic component, transfer of the alkyl groups results. With diethylbenzenes reaction occurs substantially according to the equation:

$$C_6H_4(C_2H_5)_2 + C_6H_6 \xrightarrow{AlCl_3} 2C_6H_5C_2H_5$$

Transfer of methyl groups proceeds less readily. With longer-chained alkyl groups cleavage, cracking, and transfer of the cracked fragments occur.

[11] F. Mauthner, *J. prakt. Chem. (2)*, 115, 314-330 (1926), *C. Z.*, 1928 I, 2345; *ibid.*, 121, 255-265 (1929), *C. Z.*, 1929 II, 34; *ibid.*, 136, 205-212 (1933), *C. Z.*, 1933 I, 2678; *ibid.*, 136, 213-216 (1933), *C. Z.*, 1933 I, 2679; *ibid.*, 139, 293-295 (1934), *C. A.*, 28, 3723. N. Mauthner, *Math. naturw. Ans. ungar. Akad Wiss.*, 50, 468-476 (1933), *C. A.*, 28, 3392.

[12] O. N. Witt and O. Braun, *Ber.*, 47, 3216-3232 (1914), *J. Chem. Soc. Abs.*, 108 (I), 414 (1915).

[13] R. W. Stoughton, *J. Am. Chem. Soc.*, 57, 202-204 (1934)

[14] K. von Auwers and W. Mauss, *Ann.*, 464, 293-311 (1928); *Brit. Chem. Abs.-A*, 1013 (1928).

* See page 712.

According to Boedtker and Halse,[15] the reversibility of the Friedel-Crafts reaction is shown by the fact that when polyalkylated benzenes are heated with benzene and aluminum chloride, monoalkyl derivatives are formed. The following reactions were secured by heating the indicated reactants under reflux for about six hours:

Initial Alkylated benzene	Benzene (g)	$AlCl_3$ (g)	Product
100 g *m*-xylene	1000	10	no toluene
100 g *p*-xylene	1000	10	no toluene
85 g diethylbenzene	850	20	70 g ethylbenzene
65 g mixed polyisopropylbenzenes	650	15	49 g isopropylbenzene
22 g poly-*tert*-butylbenzenes	220	5	5 g *tert*-butylbenzene
p-*tert*-dibutylbenzene	50	0.35	6.5 g *tert*-butylbenzene
mixed poly-*tert*-amylbenzenes	110	1	3 g *tert*-amylbenzene
150 g comm. *p*-isopropyltoluene	1000	30	52 g toluene 75 g isopropylbenzene
100 g *p*-isopropyltoluene	1000	20	41 g toluene 85 g isopropylbenzene

The demethylation of xylene, by boiling for two hours with 4 per cent of aluminum chloride a mixture of molecular amounts of benzene and xylene, has been attempted.[16] There was secured 860 cc of material boiling below 140°, but separation into 5° fractions showed no accumulation in the neighborhood of the boiling point of toluene. According to Orlov and Vaisfeld,[17] addition of benzene does not favor demethylation of xylene in the presence of aluminum chloride at the boiling point. Addition of trimethylbenzene leads to increased formation of products of high boiling point.

The fact that transfer of alkyl groups from polyethylated benzenes to benzene occurs upon treatment with aluminum chloride has been utilized by Cline and Reid [18] in the preparation of ethylbenzene in excellent yield. Reaction was effected by introducing, during two hours, 3 equivalents of ethylene into a mixture of 300 g of benzene, 100 g of higher ethylated benzene, 15 g of aluminum chloride, and the lower layer previously secured from the ethylation of benzene with ethylene and aluminum chloride. During the introduction of the olefin the temperature was held at 70-80°, and stirring was effected by a Witt stirrer running at 11,000 r.p.m. Seven runs were made; averages for products obtained were: recovered benzene 29 g, ethylbenzene 215 g, diethylbenzene 105 g, residue 39 g.

Attempts have been made to methylate naphthalene by heating it with polymethylbenzene in the presence of aluminum chloride.[19] Naph-

[15] E. Boedtker and O. M. Halse, *Bull. soc. chim.*, 19, 444-449 (1916); *C. A.*, 11, 938.
[16] F. Fischer and H. Niggemann, *Ber.*, 49, 1475-1482 (1916); *C. A.*, 11, 947.
[17] N. N. Orlov and P. G. Vaisfeld, *J. Applied Chem. (U. S. S. R.)*, 10, 861-868 (1937); *Brit. Chem. Abs.*-A II, 330 (1937).
[18] R. L. Cline and E. E. Reid, *J. Am. Chem. Soc.*, 49, 3150-3156 (1927).
[19] H. Niggemann, *Ges. Abhand. Kennt. Kohle*, 1, 255-258 (1917); *C. Z.*, 1919 II, 584-585.

thalene, boiled with xylene in the presence of aluminum chloride, gave indefinite mixtures of various boiling points with no definite indication of methylation of the naphthalene at the expense of the xylene.

According to Milligan and Reid,[20] naphthalene may be readily ethylated by stirring it vigorously with polyethylbenzenes and aluminum chloride at 80°. Propylation of naphthalene may be effected by stirring diisopropylbenzene with naphthalene at 90° for 4½ hours.[21]

The dealkylation of polycyclohexylbenzenes has been studied by Corson and Ipatieff.[22] Di-, tri-, and tetracyclohexylbenzenes were dealkylated to lower derivatives by the action of benzene in the presence of aluminum chloride. 1,4-Dicyclohexylbenzene and 1,3,5-tricyclohexylbenzene were thus converted to monocyclohexylbenzene. 1,2,3,5-Tetracyclohexylbenzene was dealkylated to monocyclohexylbenzene and 1,3,5-tricyclohexylbenzene. Nametkin and Pokrovskaya [23] report that reaction of cyclohexylbenzene with benzene and aluminum chloride yields 1,3- and 1,4-dicyclohexylbenzene, as well as some 1,3,5-tricyclohexylbenzene Since the latter compound was also formed by reaction of 1,4-dicyclohexylbenzene with benzene and aluminum chloride, these investigators suggest that an isomerization occurs when the third cyclohexyl group enters the ring.

Transfer of alkyl groups from alkylated phenols to benzene occurs when *p-tert*-butyl, *p-tert*-amyl, or 4-(1,1,3,3-tetramethylbutyl)phenol is treated with benzene and aluminum chloride. When 0.5 mole of *p-tert*-butylphenol, 0.66 mole of aluminum chloride, and 150 cc of benzene are refluxed for eight hours, a 70 per cent yield of *tert*-butylbenzene is secured. Corresponding quantities of reactants were used in transfer of the *tert*-amyl group from phenol, but the reaction was effected by allowing the mixture to stand at room temperature for 12 hours. A 25 per cent yield of *tert*-amylbenzene is thus obtained. Similar treatment of 4-(1,1,3,3-tetramethylbutyl)phenol results in cleavage and cracking of the octyl group, with subsequent addition of the C_4 segments to benzene. Reaction in the cold gives a 50 per cent yield of *tert*-butylbenzene; by heating, a 70 per cent yield of the same compound is secured.[24]

Halogen Migration

von Dumreicher [25] found that bromobenzene in the presence of aluminum chloride undergoes reaction to yield benzene and dibromobenzene; a considerable quantity of unreacted bromobenzene and some tarry material were also obtained.

Friedel and Crafts [26] noted that transfer of chlorine occurs during methylation of *o*-dichlorobenzene. When a heated mixture of the halo-

[20] C. H. Milligan and E. E. Reid, *J. Am. Chem. Soc.*, 44, 206-210 (1922).
[21] T. M. Berry and E. E. Reid, *J. Am. Chem. Soc.*, 49, 3142-3149 (1927); *C. A.*, 22, 394.
[22] B. B. Corson and V. N. Ipatieff, *J. Am. Chem. Soc.*, 59, 645-647 (1937); *C. A.*, 31, 3835
[23] S. S. Nametkin and E. S. Pokrovskaya, *J. Gen. Chem. (U. S. S. R.)*, 7, 962-972 (1937); *C. A.*, 31, 5332.
[24] R. A. Smith, *J. Am. Chem. Soc.*, 59, 899-900 (1937). R. A. Smith and C. J. Rodden, *J. Am. Chem. Soc.*, 59, 2333 (1937).
[25] O. von Dumreicher, *Ber.*, 15, 1566-1570 (1882).
[26] C. Friedel and J. M. Crafts, *Ann. chim. phys. (6)*, 10, 411-434 (1887); *J. Chem. Soc. Abs.*, 52, 1101 (1887).

genated benzene with 20 per cent of aluminum chloride was treated with a current of dry methyl chloride for about ten hours, the chief products were found to be hexamethylbenzene and trichloromesitylene.

A similar phenomena was seen to occur during treatment of *p*-dibromobenzene with methyl chloride in the presence of aluminum chloride.[27] Although the halogenated benzene was mainly converted into carbonaceous material, there was also formed a mixture consisting of monobromobenzene, *m*- and *p*-dibromobenzenes, and two tribromobenzenes. Obviously the aluminum chloride tends to dehalogenate the *p*-dibromobenzene to the monobromo- derivative, and the freed bromine then reacts with the monobromobenzene present to yield *m*-dibromobenzene and with the dehalogenated benzenes present to yield the tribromo- derivatives.

In 1886, Roux [28] found that, when α-bromonaphthalene is heated with 15-20 per cent of aluminum chloride at 44° for about an hour, the mixture blackens very much and β-bromonaphthalene is formed, together with some tarry substances, a small amount of naphthalene, and dibromonaphthalenes. α-Chloronaphthalene was found to be similarly effected. Under like conditions, iodine is set free from α-iodonaphthalene; conversion to the β-isomer does not occur. When a mixture of α-bromonaphthalene and toluene was heated with aluminum chloride, naphthalene and a mixture of bromotoluenes was formed, and an analogous reaction was found to occur when toluene was replaced by benzene.

Fisher and Clark [29] have found that the conversion of α-bromonaphthalene to the β-isomer in the presence of aluminum chloride is increased by the addition of several metals, notably antimony, molybdenum, nickel, and tungsten.

Lohfert [30] observed halogen migration when preparing acetyl-1,2-dibromonaphthalene from 1,2-dibromonaphthalene and acetyl chloride in the presence of aluminum chloride. Only a small amount of the desired product was obtained, the products being mainly 1,4-dibromonaphthalene and 1,5-dibromonaphthalene. It appears that the acetyl chloride gives off the hydrogen chloride required for the reaction; for a similar migration can be obtained by passing hydrogen chloride into a boiling carbon disulfide solution of dibromonaphthalene and aluminum chloride. The product is usually 2,6-dibromonaphthalene, although the 1,5-isomer is also formed in some cases. Some doubt was cast on these results by Zalkind and Stetzuro,[31] who stated that the 1,2-dibromonaphthalene used by Lohfert was actually a mixture of the 1,4- and 1,5-isomers.

Migration may also be observed when bromobenzene is heated with aluminum chloride.[32] Condensation and pyrogenic decomposition also occurs with the formation of carbon and bromine derivatives of naphthalene, anthracene, etc. The migration of bromine can reach 83 per cent

[27] A. J. Leroy, *Bull. soc. chim.*, 48, 210-216 (1887); *J. Chem. Soc. Abs.*, 54, 258 (1888).
[28] L. Roux, *Bull. soc. chim.* (2), 45, 510-521 (1886); *J. Chem. Soc. Abs.*, 50, 806 (1886).
[29] H. E. Fisher and R. H. Clark, *Can. J. Research*, 17, 251-252 (1939).
[30] H. Lohfert, *Ber.*, 63, 1939-1941 (1930); *C. A.*, 25, 100.
[31] Yu. Zalkind and Z. Stetzuro, *Ber.*, 64, 953-954 (1931); *C. A.*, 25, 3955.
[32] M. Copisarow and C. N. H. Long, *J. Chem. Soc.*, 119, 442-447 (1921); *C. A.*, 15, 2072.

if the benzene formed is removed continuously by a current of hydrogen chloride or hydrogen. Phenol promotes migration, but secondary reactions complicate the process. Since aluminum chloride and aluminum bromide have no such effect on chlorobenzene and bromobenzene, respectively, the authors conclude that, in order to avoid side-reactions in Friedel-Crafts condensations in which halogen derivatives of benzene are employed, chloro- derivatives of benzene must be used with aluminum chloride.

Kohn and co-workers [33] have studied the migration of halogen from phenols to aromatic hydrocarbons in the presence of aluminum chloride. Thirty-five g of tribromophenol in benzene treated with aluminum chloride or preferably aluminum chloride containing some ferric chloride gave 20-24 g of bromobenzene and 2-5 g of phenol. Trichlorophenol under the same conditions did not give any indication of halogen migration, whereas *p*-bromophenol gave only a slight amount of bromobenzene.[34] Replacing the benzene with toluene at 100° gave phenol and *m*-bromotoluene, but at a temperature of 130-140° the yield of bromotoluene is markedly decreased. *p*-Bromophenol with toluene gives *m*-bromotoluene and phenol.[35] From 35 g of tribromophenol and 90 g of toluene with 35 g of aluminum chloride for three hours on a water-bath there was secured 40 g of practically pure *m*-bromotoluene and 8 g of phenol.[36]

Increasing the quantity of halogen in the phenol to tetra- or pentabromophenols indicates that treatment with benzene and aluminum chloride will remove the *ortho-* and *para-* bromine atoms, forming bromobenzene and *m*-bromophenol.[37] With bromochlorophenols there is preferential debromination. Thus 2,4-dichloro-3,5,6-tribromophenol reacts with aluminum chloride and benzene forming 2,4-dichloro-3,5-dibromophenol and bromobenzene;[38] whereas 3-chloro-2,4,5,6-tetrabromophenol may be debrominated to yield 3-chloro-5-bromophenol.[39]

Cresols behave like phenols in these migration tendencies. Tetrabromo-*o*-cresol heated with benzene and aluminum chloride gives bromobenzene and 4,6-dibromo-*o*-cresol. 3,5-Dibromo-*o*-hydroxybenzyl bromide with benzene and aluminum chloride gives not a normal Friedel and Crafts reaction to a diphenylmethane derivative, but phenol and bromobenzene.[40] Tetrabromo-*p*-cresol treated in a similar manner yields 2,6-dibromo-*p*-cresol. 2,3,5-Tribromo-*p*-cresol is debrominated completely to *p*-cresol, none of the expected *o*-bromocresol being formed. 3,5-Di-

[33] M. Kohn and F. Bum, *Monatsh.*, 33, 923-928 (1912); *J. Chem. Soc. Abs. (I)*, 760 (1912). M. Kohn and A. Fink, *Monatsh.*, 44, 183-195 (1924); *J. Chem. Soc. Abs. (I)*, 133 (1925). M. Kohn and M. Jawets, *Monatsh.*, 44, 197-207 (1924); *J. Chem. Soc. Abs. (I)*, 135 (1925). M. Kohn and J. Wiesen, *Monatsh.*, 45, 251-259 (1925); *J. Chem. Soc. Abs. (I)*, 539 (1925). M. Kohn and M. Weisberg, *Monatsh.*, 45, 295-302 (1925); *J. Chem. Soc. Abs. (I)*, 655 (1925). M. Kohn and N. L. Müller, *Monatsh.*, 30, 407-409 (1909), *C. A.*, 4, 309. M. Kohn, *Monatsh.*, 32, 105-111 (1911); *C. A.*, 25, 4536. M. Kohn and A. Zandman, *Monatsh.*, 47, 357-377 (1926); *Brit. Chem. Abs.-A*, 52 (1927). M. Kohn and G. Dömötör, *Monatsh.*, 47, 207-240 (1926); *Brit. Chem. Abs.-A*, 51 (1927).

[34] M. Kohn and N. L. Müller, *Monatsh.*, 30, 407-409 (1909); *C. A.*, 4, 309.

[35] M. Kohn, *Monatsh.*, 33, 923-928 (1912); *C. A.*, 6, 2180 (1912).

[36] M. Kohn and A. Fink, *Monatsh.*, 44, 183-195 (1924); *J. Chem. Soc. Abs. (I)*, 133 (1925).

[37] M. Kohn and G. Dömötör, *Monatsh.*, 47, 207-240 (1926); *Brit. Chem. Abs.-A*, 51 (1927).

[38] M. Kohn and A. Zandman, *Monatsh.*, 47, 357-377 (1926); *Brit. Chem. Abs.-A*, 52 (1927).

[39] M. Kohn and M. Jawets, *Monatsh.*, 44, 197-207 (1924); *J. Chem. Soc. Abs. (I)*, 135 (1925).

bromo *p*-hydroxybenzyl bromide gives *p*-cresol, probably by way of the dibromodiphenylmethane derivative.[41] Tetrabromo-*m*-cresol on treatment with benzene and aluminum chloride forms 5-bromocresol.[42] Tetrabromo-*o*-cresol yields 4,6-dibromo-o-cresol under similar treatment.[43] Bis-(*p*-hydroxyphenyl)-dimethylmethane gives a tetrabromo- derivative which yields phenol and bromobenzene on treatment with benzene and aluminum chloride. Tribromoresorcinol also yields phenol and bromobenzene under similar conditions.[44]

In connection with this study of halogenated phenols it may be pointed out that Copisarow and Long,[32] in their study of halogen migration in dibromobenzene, attempted to fix the nascent halogen by substituting phenol for the benzene and obtained tribromophenol. There is no doubt that halogen migrations are equilibrium reactions if we compare the work of Copisarow and Long mentioned above with that of Kohn and Müller.[34]

In the case of the repellant action in dihalogenated cyclohexane Nenitzescu and Curcăneanu [45] obtained by the reaction of benzene and 1,2-dihalogenated cyclohexane considerable 1,2-diphenylcyclohexane, a lesser quantity of the 1,3-isomer, a still smaller quantity of the 1,4-isomer, and also cyclohexylbenzene. Halogen substituents, therefore, may not repel another halogen to the farthest possible position.

Halogen migration has been shown to occur with certain halogenated ketones, acids, and ethers. Cyclohexene adds acetyl chloride in the presence of aluminum chloride to form 1-chloro-2-acetylcyclohexane. Nenitzescu and Gavăt [46] found that the phenyl group, when treated with benzene, does not enter the *ortho*-position, but that 1-phenyl-4-acetylcyclohexane is the final product. Under the influence of aluminum chloride the chlorine atom has migrated from the 2- to the 4-position. In like manner cyclopentene yields 1-phenyl-3-acetylcyclopentane by reaction with acetyl chloride and benzene. The keto-group present exerts the repelling action.

2-Butene adds acetyl chloride, and this reacts with benzene to yield 3-methyl-4-phenylpentan-2-one. No migration occurs. However, under the same conditions 1-butene yields 5-phenylhexan-2-one. It appears that by the action of aluminum chloride the chlorine atom in the chain or the ring of a chlorinated ketone migrates to a position farthest from the carbonyl group; however, it cannot migrate to the end methyl group. Like conclusions are drawn from the reactions of carboxylic acids and ethers.

Migration and elimination of iodine occurs upon treatment of 1-iodo-2,4-dimethoxybenzene with aluminum chloride, the products being 1,5-diiodo-2,4-dimethoxybenzene and *m*-dimethoxybenzene. Obviously migration of iodine is more readily effected than alkoxy- cleavage.[47]

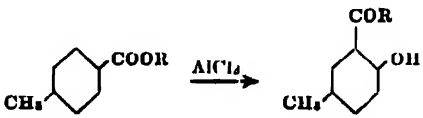
[41] M. Kohn and J. Wiesen, *Monatsh.*, 45, 251-259 (1925); *J. Chem. Soc. Abs. (1)*, 539 (1925).
[42] M. Kohn and M. Weissberg, *Monatsh.*, 45, 295-303 (1925); *J. Chem. Soc. Abs. (1)*, 655 (1925).
[43] M. Kohn and F. Rabinowitsch, *Monatsh.*, 48, 361-374 (1927); *Brit. Chem. Abs.-A*, 967 (1927).
[44] M. Kohn, *Monatsh.*, 52, 108-111 (1931); *C. A.*, 25, 4536.
[45] C. D. Nenitzescu and D. Curcăneanu, *Ber.*, 70, 346-348 (1937); *C. A.*, 31, 3457; *cf.* C. D. Nenitzescu, I. G. Gavăt, and D. Cocora, *Ber.*, 73, 233-237 (1940).
[46] C. D. Nenitzescu and I. Gavăt, *Ann.*, 519, 260-271 (1935); see also C. D. Nenitzescu, I. G. Gavăt, and D. Cocora, *Ber.*, 73, 233-7 (1940).
[47] H. Meerwein, P. Hofmann, and F. Schill, *J. prakt. chem. (2)*, 59, 266-283 (1940); *Brit. Chem. Abs.-A* II, 167 (1940).

Intermolecular migration of halogen renders it feasible to produce aromatic dicarboxylic acid chlorides from the acid anhydrides and an organic halide in the presence of aluminum chloride. Mares produced phthaloyl chloride by the reaction of phthalic anhydride and carbon tetrachloride.[48] Benzoyl trichloride, or its homologs or substitution products, may be similarly used as the chlorinating agent.[49] Halogen exchange is used in the preparation of halogen-containing vat dyes of the dibenzanthrone series. The catalyst acts as the halogenating agent if no organic halide is present.[50] It may be concluded from the reactions of halogenated hydrocarbons that:

1. Chlorine atoms are more firmly attached to the ring than bromine atoms.
2. Halogen substituents are set free as nascent atoms which are very reactive and thus account for the anomalous behavior of halogenated hydrocarbons.
3. The influence of a hydroxy-group is to loosen the halogen-to-ring bond of bromine atoms *ortho-* and *para-* to the hydroxy group, permitting them to become nascent and thus accounting for their entering a different position.
4. Halogen atoms may shift their position on the ring during the Friedel-Crafts reaction to a position farther removed from any other negative groups present. The repulsing action of halogen is less than that of carbonyl and ether groups.

Fries Rearrangement *

The rearrangement of phenolic esters to hydroxy- aromatic ketones by means of aluminum chloride



was first noted by Fries and Finck.[51]

Rosenmund and Schnurr [52] have made an extensive study of this reaction. When 10 g of phenyl benzoate and 8 g of aluminum chloride were heated together for 15 minutes at 140°, a quantitative yield of *p*-hydroxybenzophenone was obtained. The amount of aluminum chloride used was slightly in excess of molecular proportions.

Although aluminum chloride is the most effective catalyst in carrying out Fries rearrangements, anhydrous ferric chloride and especially zinc

[48] U. S. P. 2,051,096 (1936) to J. R. Mares (to Monsanto Chemical Co.).
[49] U. S. P. 1,868,749 (1934) to L. P. Kyrides (to Monsanto Chemical Co.), *C. A.*, **26**, 5079. Brit P. 414,570 to Monsanto Chemical Co. (1933).
[50] Brit. P. 351,048 (1930) to I. G.; *Brit. Chem. Abs.*-B, 1041 (1931).
* See A. H. Blatt, *Chem. Reviews*, **27**, 413-26 (1940) for a comprehensive review of this reaction
[51] K. Fries and G. Finck, *Ber.*, **41**, 4271-4284 (1908); *J. Chem. Soc. Abs.*, **96** (I), 43 (1909).
[52] K. W. Rosenmund and D. Schnurr, *Ann.*, **460**, 56-98 (1928); *Brit. Chem. Abs.*-A, 1010 (1928)

chloride are only slightly less efficient.[53] According to Sekera,[54] other catalysts than aluminum chloride are less effective in this rearrangement.

There has been some difference of opinion regarding the mechanism of this reaction.

Fries,[55] Witt,[56] and von Auwers[57] considered the reaction to be intramolecular.

Skraup and Poller[58] suggested the intermediate formation of acetyl chloride in the preparation of *o*-acetyl-*m*-cresol from *m*-tolyl acetate through decomposition of the ester by the zinc chloride which they used as catalyst and its subsequent reaction with the cresol to form the ketone.

If the reaction is not a molecular rearrangement, but a saponification and resubstitution, von Auwers and Mauss[59] postulated that a mixture of phenyl acetate and *p*-tolyl chloroacetate with aluminum chloride should give six different ketones, the *o*-acetyl- and *o*-chloroacetyl derivatives of phenol and cresol, as well as *p*-acetyl- and *p*-chloroacetylphenol, whereas molecular rearrangement should produce only *o*- and *p*-acetylphenyl and 4,2-methylchloroacetylphenol. The actual product of the reaction was *o*-acetylphenol.

The Fries reaction has been contrasted[60] with Friedel-Crafts acylation of phenols. Since the Friedel-Crafts reaction on most phenols in the preparation of aromatic hydroxy- ketones generally gives the *p*-acyl phenols[61] and, with a few phenol ethers of certain structure, the *meta* derivatives, and since in the Fries reaction only *ortho*- or *para*- and never *meta*-acyl phenols are produced, the Fries reaction was considered to take place *within the molecule*.

Rosenmund and Schnurr[62] considered the Fries reaction from two viewpoints—as a true Friedel-Crafts reaction or as the intramolecular change suggested by von Auwers. They found that when a mixture of *o*-chloro-*p*-tolyl acetate and *p*-tolyl benzoate is treated with aluminum chloride, four products are obtained—not only 2-hydroxy-3-chloro-5-methylacetophenone and 2-hydroxy-5-methylbenzophenone, but also 2-hydroxy-3-chloro-5-methylbenzophenone and 2-hydroxy-5-methylacetophenone. A strictly intramolecular reaction should give only the first two compounds. On the other hand, when the mechanism of the Fries change has been interpreted as involving two molecules of the ester it thus resembles the Friedel-Crafts reaction where acetic acid is the acetylating agent.

[53] J. F. Eijkmann, *Chem. Weekblad*, 1, 453-461 (1904), *J. Chem. Soc. Abs.*, 86 (I), 664 (1904). G. Heller, *Ber.*, 42, 3736-3742 (1909), *C. A.*, 3, 2690; *ibid.*, 45, 418-427 (1912), *C. A.*, 6, 1298; *ibid.*, 45, 2389-2392 (1912), *C. A.*, 7, 88.

[54] V. C. Sekera, *Trans. Illinois State Acad. Sci.*, 27, 81-82 (1935); *Brit. Chem. Abs.-A*, 55 (1936).

[55] K. Fries and G. Finck, *loc cit.* K. Fries and W. Pfaffendorf, *Ber.*, 43, 212-219 (1910); *C. A.*, 4, 1046. K. Fries and R. Fröllstedt, *Ber.*, 54, 715-725 (1921); *C. A.*, 15, 2873. K. Fries and H. Ehlers, *Ber.*, 56, 1304-1308 (1923); *C. A.*, 17, 3333.

[56] O. N. Witt and O. Braun, *Ber.*, 47, 3216-3232 (1914); *J. Chem. Soc. Abs.*, 108 (I), 1414 (1915).

[57] K. v. Auwers and W. Mauss, *Ann.*, 464, 293-311 (1928); *Brit. Chem. Abs.-A*, 1013 (1928).

[58] S. Skraup and K. Poller, *Ber.*, 57, 2033-2038 (1924); *C. A.*, 19, 1257.

[59] K. v. Auwers and W. Mauss, *Ber.*, 61, 416-421 (1928); *C. A.*, 22, 1762.

[60] K. v. Auwers and W. Mauss, *Ber.*, 61, 1495-1507 (1928); *C. A.*, 22, 4490. See also page 351.

[61] K. v. Auwers and W. Mauss, *Ann.*, 464, 293-311 (1928); *Brit. Chem. Abs.-A*, 1013 (1928).

[62] K. W. Rosenmund and W. Schnurr, *Ann.*, 460, 56-96 (1928); *Brit. Chem. Abs.-A*, 1010 (1928).

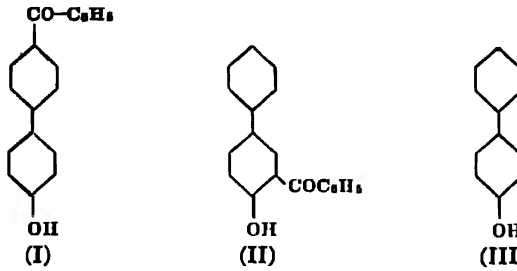
This conclusion that the Fries reaction is bimolecular in type has been questioned by von Auwers [61] When mixtures of phenol esters of different acids are submitted to Fries conditions, exchange of acyl groups frequently takes place, the course of the reaction being determined by the nature of the substances concerned (the benzoyl and chloroacetyl groups are more firmly attached to oxygen than is the acetyl group). When a mixture of 2-hydroxymesityl methyl ether and *p*-tolyl chloroacetate was heated with aluminum chloride, the two free phenols, chloroacetic acid, and unchanged ether were the sole products. Had Rosenmund substitution occurred, ketones derived from the ethers should have been formed The reciprocal change of acyl groups was further shown when the acetate of 2-hydroxymesitylene and 3-chloro-*p*-tolyl benzoate with aluminum chloride gave free phenols, 3-chloro-2-hydroxy-5-methylacetophenone, the corresponding -benzophenone, and the benzoate of 2-hydroxymesitylene It is thus concluded by von Auwers that the Fries transformation is an intra- and not an intermolecular change.

The experimental work of Cox [63] supports the conclusion that the Fries reaction is not intramolecular. When phenolic esters are acted upon by anhydrous aluminum chloride in the presence of an acceptor, as diphenyl ether, the free acid chlorides are produced as intermediates which are then introduced into the acceptor, giving ketones Skraup and Poller [64] had previously proposed this mechanism with zinc chloride as catalyst. If an intramolecular change took place it should be possible to isolate the intermediate formed; the failure to identify such a product and the work of Rosenmund and Schnurr [62] are contrary to the intramolecular reaction theory.

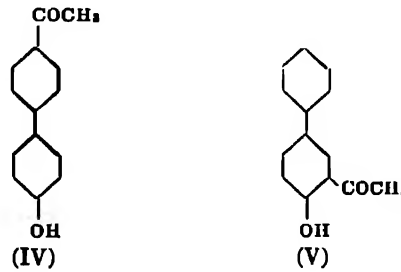
There is no change of free radicals since a catalyst is necessary for the transformation. This is borne out by the fact that, although Skraup and Beng [65] obtained very low yields of ketones by pyrolysis of special phenyl esters such as phenyl β,β-dimethylacrylate, in the presence of zinc chloride and halogen acids lower temperatures are permitted and higher yields of ketones may thus be obtained.

The case for intermolecular mechanism is again brought out in several reported instances of heterogeneous migration of biphenyl esters Blicke and Weinkauff [66] have secured 4-hydroxy-4'-benzoylbiphenyl (I) by heating the benzoate of 4-hydroxybiphenyl in tetrachloroethane solution for one hour at 140°. Using the same amount of reactants and the same reaction conditions, Hey and Jackson [67] secured 3-benzoyl-4-hydroxybiphenyl (II) together with some 4-hydroxybiphenyl (III) In carbon disulfide solution, Fieser and Bradsher,[68] however, obtained the same product as that reported by Blicke and Weinkauff.

[61] E. H. Cox, *J. Am Chem. Soc.*, 52, 352-358 (1930); *Brit. Chem. Abs.*-A, 344 (1930).
[62] S. Skraup and K. Poller, see Note 58.
[63] S. Skraup and F. Beng., *Ber.*, 60, 942-950 (1927); *C A.*, 21, 2125
[64] F. F. Blicke and O. J. Weinkauff, *J. Am. Chem. Soc.*, 54, 330-334 (1932); *C. A.*, 26, 931.
[65] D. H. Hey and E. R. B. Jackson, *J Chem. Soc.*, 802-806 (1936); *C. A.*, 30, 5964.
[66] L. F. Fieser and C. K. Bradsher, *J. Am. Chem. Soc.*, 58, 2337-2338 (1937); *C. A.*, 31, 288.



In the rearrangement of the acetate of 4-hydroxybiphenyl in carbon disulfide, Bradsher had previously found that the acetyl group migrates to both the *ortho* and the *para* positions, the products obtained being 4-hydroxy-4′-acetylbiphenyl (IV) and 3-acetyl-4-hydroxybiphenyl (V):



The work on biphenyl esters cited above illustrates the perversity of Fries rearrangements and also confirms a mechanism involving cleavage of ester to the free phenol and subsequent acylation of the phenol in another nucleus, indicating again that the Fries reaction is not a true rearrangement but an intermolecular acylation.

The absence of the Fries rearrangement in the case of 5-acetoxy-2-methyl-3-acetylchromone and of 7-acetoxy-2-methyl-3-acetylchromone has been attributed by Kelkar and Limaye [69] to the retarding influence of the acyl group in the 3-position, since chromones without the acyl group in position 3 rearrange normally. Because of this inhibiting effect Fries rearrangement does not take place and only hydrolysis results.

2,4,6-Trichlorophenyl acetate was found [91] to give no ketone even when heated for four hours at 130-140° in the presence of excess aluminum chloride. This may be caused by blocking of the *ortho* and *para* position by the immobile chlorine atoms.

von Auwers and co-workers [70] have studied the migration of the alkyl groups during Fries rearrangements.

The conversion of phenolic acetates into *o*- and *p*-hydroxyacetyl-

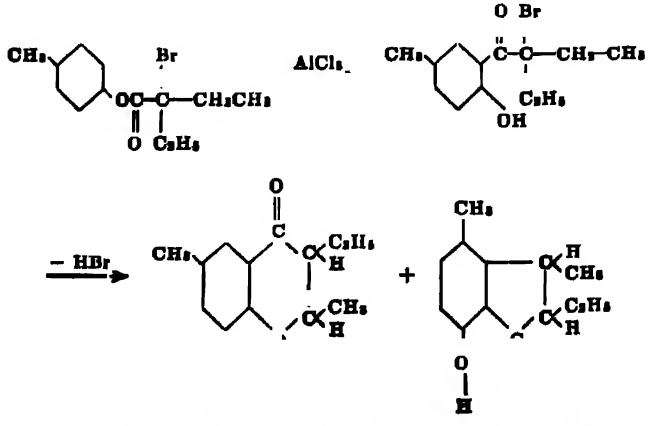
[69] G. R. Kelkar and D. B. Limaye, *Resayanam*, 1, 60-64 (1936); *C. Z.*, 1937 I, 2598.
[70] K. v. Auwers, H. Bundesmann, and F. Wieners, *Ann.*, 447, 162-196 (1926); *Brit. Chem. Abs.*-A, 608 (1926). K. v. Auwers and W. Mauss, *Ann.*, 460, 240-277 (1928); *Brit. Chem. Abs.*, A, 417 (1928). K. v. Auwers and E. Janssen, *Ann.*, 483, 44-65 (1930); *C. A.*, 25, 929. K. v. Auwers and W. Mauss, *Ber.*, 61, 1695-1707 (1928); *C. A.*, 22, 4490.

phenones by heating with aluminum chloride is accompanied, in the case of certain polyalkyl phenols, by migration of an alkyl group. This migration takes place only when the acetyl group migrates to the *o*-position, and then only when the 2- and 5- and 3,6-positions are occupied by alkyl. The position next to the ketone group remains unoccupied in the final product.

Direction of the keto migration to the *ortho*- position is favored by *meta*-alkyl groups. The ethyl group is more easily shifted than the methyl group, as is shown by the fact that the ethyl group rather than the methyl group is shifted when both occupy *ortho*- positions. The ethyl group usually migrates to the *para*- position relative to the position it originally occupied. No shifting of the *ortho*-ethyl group occurs when the keto group enters the *para*- position. When forced to migrate, the methyl group may displace an ethyl group. The ease of migration of different groups is in the order ethyl > propyl > methyl.

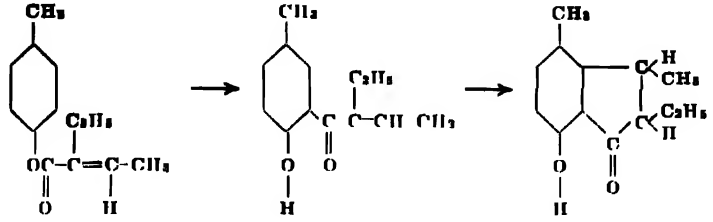
Migration of the acyl group to the *para*- position is favored by mild conditions, and to the *ortho*- position by drastic conditions. The rate of migration is increased by raising the temperature. For example Rosenmund and Schnurr [62] found that in the cold one day was necessary for thymyl acetate to change to the ketone, whereas at 60° the reaction is complete in ten minutes. Aromatic acyl radicals migrate with much less rapidity, as is shown in the reaction of thymyl benzoate and carvacryl benzoate. The rates of migration into the *para*- position of some acyl radicals in the case of thymol esters is given as acetyl, propionyl > phenylacetyl, phenylpropionyl, β-phenylacrylyl > benzoyl. Migration of acyl groups to the *ortho*- position is more rapid when the *para*- position is blocked.

Ring closure occurs in some instances during Fries reactions, with production of coumaranones and hydrindones. *p*-Tolyl α-bromo-α-ethylbutyrate [71] produces a mixture of 2,6-dimethyl-3-ethyl coumaranone and 2-ethyl-3,4-dimethyl-7-hydroxyhydrindone as follows:

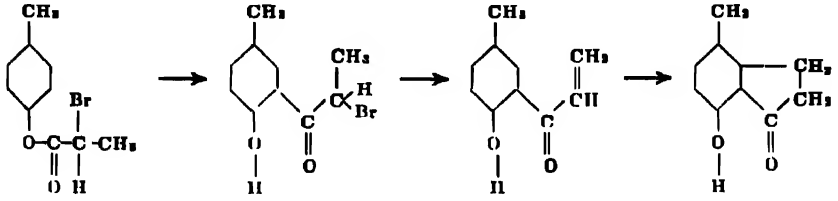


[71] K. v. Auwers, *Ann.*, **439**, 132-175 (1924); *J. Chem. Soc. Abs.*, **126** (I), 1219 (1924).

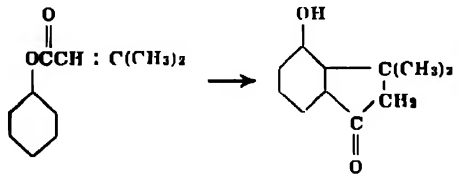
and *p*-tolyl α-ethylcrotonate yields 7-hydroxy-3,4-dimethyl-2-ethyl hydrindone:



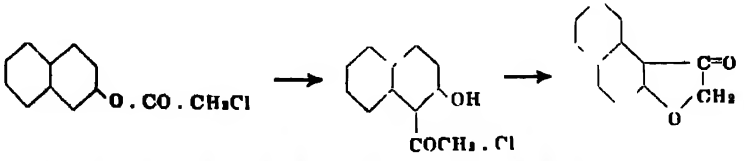
In studying the formation of hydroxy hydrindones by the reaction of *p*-tolyl α-bromopropionate and aluminum chloride von Auwers [72] states that it is probable that *p*-cresyl vinyl ketone is formed as an intermediate product. His reaction would go as follows to produce the hydrindone:



When phenyl β,β-dimethacrylate was heated with aluminum chloride, von Auwers and Mauss [73] obtained *o*-hydroxy-3,3-dimethylhydrindone:

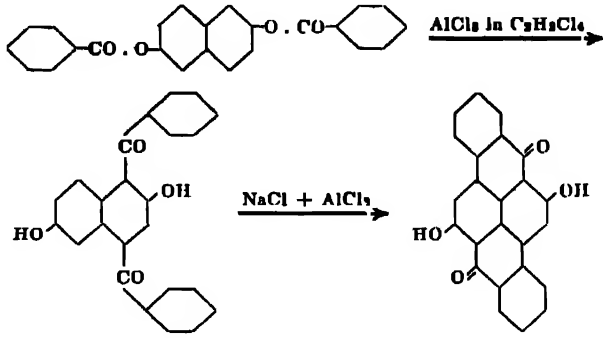


The formation of 4,5-benzocoumaranone-(3) from β-naphthyl chloroacetate involves Fries rearrangement and subsequent ring-closure [74]:

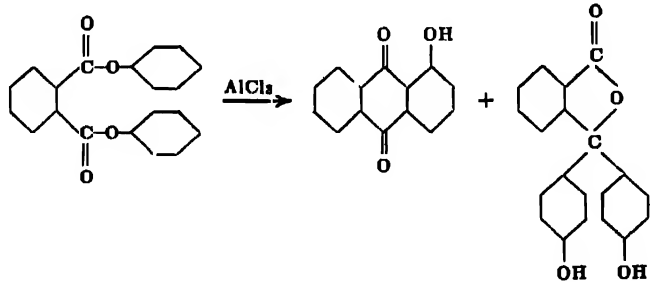


[72] K. v. Auwers, *Ber.*, 44, 3092-3099 (1911); *J. Chem. Soc. Abs.*, 102 (I), 107 (1912).
[73] K. v. Auwers and W. Mauss, *Ber.*, 61, 416-421 (1928); *C. A.*, 22, 1762.
[74] K. Fries and R. Frellstedt, *Ber.*, 54, 715-725 (1921).

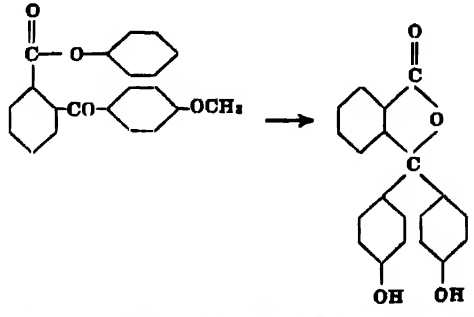
Fries rearrangement may be accompanied by Scholl intramolecular ring-closure [75]:



Although a true Fries rearrangement cannot take place with the diphenyl esters of phthalic and naphthalic acids because of the proximity of the —COOAr groups on the nucleus, rearrangement and ring closure take place. Diphenyl phthalate is converted to 1-hydroxyanthraquinone (23-33 per cent) and phenolphthalein (63 per cent);[76]

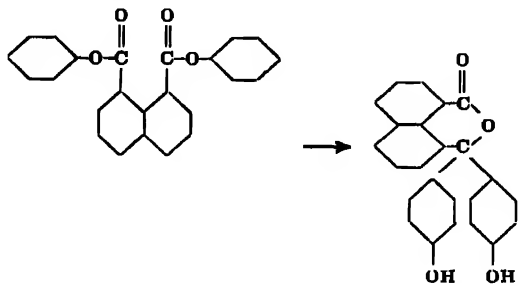


similarly phenyl 2-(*p*-methoxybenzoyl)benzoate is changed, practically quantitatively, into phenolphthalein:



[75] German P. 455,955, German P. 453,280, British P. 248,791 to I. G. Farbenindustrie; *C. Z.*, 1927 II, 336.
[76] F. F. Blicke and O. J. Weinkauff, *J. Am. Chem. Soc.*, 54, 330-334 (1932).

Diphenyl naphthalate gave a 40 per cent yield of phenolnaphthalein.[77]



The following table illustrates Fries rearrangements.

(*Text cont'd on p.* 709)

Table 33

Ketone	% Yield	Ester	Ref.
o-Acetylphenol	30	phenyl acetate	10, 23, 34, 35
p-Acetylphenol		phenyl acetate	34, 35
o-Hydroxy-ω-chloroacetophenone	50	phenyl chloroacetate	35
p-Hydroxy-ω-chloroacetophenone		phenyl chloroacetate	35
o-Propionylphenol	32-35	phenyl propionate	33
p-Propionylphenol	45-50	phenyl propionate	
o-*n*-Butyrylphenol	60	phenyl *n*-butyrate	
o-*n*-Hexoylphenol	50	phenyl *n*-hexoate	
o-*n*-Heptoylphenol	58	phenyl *n*-heptoate	
p-Lauroylphenol		phenyl laurate	60
p-Stearoylphenol		phenyl stearate	60
o-Hydroxy-3,3-dimethylhydrindone		phenyl β,β-dimethacrylate	8
o-Hydroxybenzophenone	26	phenyl benzoate	31
p-Hydroxybenzophenone	100	phenyl benzoate	6, 25
p-Acetyl-*o*-cresol	25	*o*-tolyl acetate	6, 10
3-*n*-Butyryl-*o*-cresol	60	*o*-tolyl *n*-butyrate	30
5-*n*-Butyryl-*o*-cresol	30	*o*-tolyl *n*-butyrate	30
p-Isobutyryl-*o*-cresol		*o*-tolyl isobutyrate	47
3-*n*-Valeryl-*o*-cresol	46	*o*-tolyl *n*-valerate	30
5-*n*-Valeryl-*o*-cresol	30	*o*-tolyl *n*-valerate	30
3-*n*-Hexoyl-*o*-cresol	60	*o*-tolyl *n*-hexoate	30
5-*n*-Hexoyl-*o*-cresol	25	*o*-tolyl *n*-hexoate	30
2,4-Methylbenzoylcresol	91	*o*-tolyl benzoate	24
4-Acetyl-*m*-cresol		*m*-tolyl acetate	6, 10
6-Acetyl-*m*-cresol		*m*-tolyl acetate	6, 10, 13, 14
ω-Chloro-2-hydroxy-4-methyl acetophenone	50	*m*-tolyl chloroacetate	1
4-Propionyl-*m*-cresol	10	*m*-tolyl propionate	4
6-Propionyl-*m*-cresol	67-93	*m*-tolyl propionate	4
4-Butyryl-*m*-cresol	5, 2	*m*-tolyl butyrate	4, 30
6-Butyryl-*m*-cresol	66-75, 88	*m*-tolyl butyrate	4, 30
7-Hydroxy-3,3-dimethylhydrindone		*m*-tolyl α-bromoisobutyrate	39

[77] F. F. Blicke and R. A. Patelski, *J. Am. Chem. Soc.*, 60, 2283-2285 (1938).

Table 33—*(Continued)*

Ketone	% Yield	Ester	Ref
5-Hydroxy-2,7-dimethylhydrindone		*m*-tolyl α-bromoisobutyrate	39
6-Valeryl-*m*-cresol	67-80, 85	*m*-tolyl valerate	4, 30
6-Hexoyl-*m*-cresol	62-91, 98	*m*-tolyl hexoate	4, 30
6-Heptoyl-*m*-cresol	67-78, 84	*m*-tolyl heptoate	4, 30
6-Nonoyl-*m*-cresol	75	*m*-tolyl pelargonate	4
Dimethyl-α,ω-dihydroxydiphenyl-diketohexane		di-(*m*-tolyl) adipate	19
5,6-Methylbenzoylcresol	50-100	*m*-tolyl benzoate	6, 24
3,4-Methylbenzoylcresol	32	*m*-tolyl benzoate	6, 24
p-Cresyl ω-methyl ketone		*p*-tolyl acetate	14
ω-Chloro-2-hydroxy-5-methyl aceto-phenone	90	*p*-tolyl chloroacetate	1
7-Hydroxy-4-methyl-1-hydrindone	40-50	*p*-tolyl α-bromopropionate	17
7-Hydroxy-3,4-dimethyl-1-hydrin-done		*p*-tolyl α-bromobutyrate	
7-Hydroxy-3,4-dimethyl-1-hydrin-done	40-50	*p*-tolyl α-bromoisobutyrate	17
3,4-Dimethyl-7-hydroxyhydrindone		*p*-tolyl crotonate	43
3,5-Dimethyl-3-ethylcoumaranone	48	*p*-tolyl α-bromo α-ethylbutyrate	30
7-Hydroxy-3,4-dimethyl-2-ethyl hydrindone		*p*-tolyl α-bromo-α-ethylbutyrate	30
7-Hydroxy-3,4-dimethyl-2-ethyl hydrindone		*p*-tolyl α-ethylcrotonate	30
4,2-Methylbenzoylcresol	94-100	*p*-tolyl benzoate	6, 24
3-Ethyl-4-acetylphenol	50	*m*-ethylphenyl acetate	32
3-Ethyl-6-acetylphenol		*m*-ethylphenyl acetate	32
2-Acetyl-3,5-dimethylphenol		3,5-dimethylphenyl acetate	7, 53
2,6-Diacetyl-3,5-dimethylphenol	small	3,5-dimethylphenyl acetate	53
6-Acetyl-3,4-dimethylphenol		3,4-dimethylphenyl acetate	7
6-Acetyl-2,4-dimethylphenol		2,4-dimethylphenyl acetate	7, 13
6-Isobutyryl-2,4-dimethylphenol	70	2,4-dimethylphenyl isobutyrate	47
ω-Chloro-2-hydroxy-3,5-dimethyl acetophenone		xylyl chloroacetate	1
6-Acetyl-2,4-dimethylphenol		2,5-dimethylphenyl acetate	7
6-Acetyl-2,3-dimethylphenol		2,3-dimethylphenyl acetate	15
4-Acetyl-2,6-dimethylphenol		2,6-dimethylphenyl acetate	13
2,6-Dimethyl-4-propionylphenol		2,6-dimethylphenyl propionate	16
2,6-Dimethyl-4-butyrylphenol		2,6-dimethylphenyl butyrate	16
2,6-Dimethyl-4-heptoylphenol		2,6-dimethylphenyl heptoate	16
2,6-Dimethyl-4-dodecylphenol		2,6-dimethylphenyl dodecoate	16
2,6-Dimethyl-4-benzoylphenol		2,6-dimethylphenyl benzoate	16
6-Acetyl-4-methyl-2-ethylphenol		4-methyl-2-ethylphenyl acetate	7
6-Acetyl-4-methyl-2-methylphenol		5-methyl-2-ethylphenyl acetate	7
4-Acetyl-2-methyl-6-ethylphenol		2-methyl-6-ethylphenyl acetate	15
6-Acetyl-2-methyl-4-ethylphenol		2-methyl-6-ethylphenyl acetate	15
2-Acetyl-3,5-diethylphenol		3,5-diethylphenyl acetate	15
4-Hydroxy-2-methyl-5-isopropyl-acetophenone		thymyl acetate	6
4-Hydroxy-2-methyl-5-isopropyl-benzophenone		thymyl benzoate	6
4-Hydroxy-5-methyl-2-isopropyl-benzophenone		carvacryl benzoate	6
2-Acetyl-3,4,5-trimethylphenol		3,4,5-trimethylphenyl acetate	7

Table 33—*(Continued)*

Ketone	% Yield	Ester	Ref.
6-Acetyl-2,3,4-trimethylphenol		2,3,4-trimethylphenyl acetate	7
6-Acetyl-2,3,4-trimethylphenol		2,4,5-trimethylphenyl acetate	7
6-Acetyl-2,3,4-trimethylphenol		2,3,5-trimethylphenyl acetate	7
6-Acetyl-2,3,4-trimethylphenol		2,4,6-trimethylphenyl acetate	7
2-Acetyl-4,5-dimethyl-6-ethylphenol		2,4-dimethyl-6-ethylphenyl acetate	15
6-Acetyl-2,4-dimethyl-3-ethylphenol		2,4-dimethyl-6-ethylphenyl acetate	15
2,4-Dimethyl-5-ethyl-6-acetylphenol		2,4-dimethyl-5-ethylphenyl acetate	15
2,4-Dimethyl-3-ethyl-6-acetylphenol		2,4-dimethyl-5-ethylphenyl acetate	15
4-Hydroxy-3,5-dimethylphenacyl chloride		2,6-dimethyl-4-ethylphenyl chloroacetate	13
6-Acetyl-2-methyl-3,4-diethylphenol		2-methyl-4,6-diethylphenyl acetate	15
6-Acetyl-2,3,4-triethylphenol		2,4,6-triethylphenyl acetate	15
4-Acetylcatechol	88	catechol diacetate and excess catechol	26
4-Chloroacetylcatechol	60	catechol monochloroacetate	26
4-Propionylcatechol	80	catechol dipropionate	26
4-Butyrylcatechol	70	catechol dibutyrate and excess catechol	26
4-*n*-Amylcatechol	50	catechol di-*n*-valerate	27
4-Isoamylcatechol	60	catechol diisovalerate	27
Isoamylcatechol	40	catechol diisovalerate	26
4-*n*-Caproylcatechol	72	catechol di-*n*-hexoate	27
4-Isocaproylcatechol	60	catechol diisohexoate	27
4-*n*-Caprylylcatechol	50	catechol di-*n*-octanoate	27
4-Benzoylcatechol	100	catechol dibenzoate	26
4-Acetylcatechol	30	guaiacol acetate	26
4-Propionylcatechol	51-55	guaiacol propionate	27
2,3-Dihydroxyphenyl ethyl ketone		guaiacol propionate	27
4-Hydroxy-3-methoxyphenyl ethyl ketone		guaiacol propionate	29, 30
4-Hydroxy-3-methoxyphenyl *n*-propyl ketone		guaiacol *n*-butyrate	29, 30
4-*n*-Butyrylcatechol	23-62	guaiacol *n*-butyrate	27, 28
4-*n*-Amylcatechol		guaiacol *n*-valerate	28, 30
2,3-Dihydroxyphenyl isobutyl ketone		guaiacol isovalerate	27
4-Isoamylcatechol		guaiacol isovalerate	28
2,3-Dihydroxyphenyl *n*-heptyl ketone		guaiacol *n*-caproate	27
4-*n*-Caproylcatechol	30-47	guaiacol *n*-caproate	27, 28, 30
4-Hydroxy-3-methoxyphenyl *n*-amyl ketone		guaiacol *n*-caproate	29, 30
2,3-Dihydroxyphenyl isoamyl ketone		guaiacol isocaproate	27
4-Isocaproylcatechol		guaiacol isocaproate	28
4-*n*-Heptoylcatechol	8-17	guaiacol *n*-heptoate	27, 28
4-Caprylylcatechol		guaiacol caprylate	28
2,6-Diacetylorcinol		orcinol diacetate	59
Quinacetophenone	54	hydroquinone diacetate and hydroquinone	26
Quinpropionylphenone	61	hydroquinone dipropionate and hydroquinone	26
Methyl 4-propionylsalicylate		propionate of methyl salicylate	8
Methyl 4-butyrylsalicylate		butyrate of methyl salicylate	8
Methyl 4-isohexylylsalicylate		isocaproate of methyl salicylate	8
Methyl 4-hexylylsalicylate		caproate of methyl salicylate	8
2,5,7,8-Tetramethyl-6-hydroxychromone	16	pseudocumohydroquinone diacetate	12 36

Table 33—*(Continued)*

Ketone	% Yield	Ester	Ref
1,3,4-Trimethyl-5-acetyl-2,6-dihydroxybenzene	42	pseudocumohydroquinone diacetate	40 36
2,5,7,8-Tetramethyl-6-acetylchromone	26	pseudocumohydroquinone diacetate	36
4-Benzoylresorcinol		resorcinyl dibenzoate	48
2,4,6-Tribenzoyl-1,3-resorcinol		resorcinyl dibenzoate	48
1-Hydroxyanthraquinone	23-33	diphenyl phthalate	25
3-(4"-Hydroxybenzoyl)-4'-hydroxybenzophenone		diphenyl isophthalate	37
4-(4"-Hydroxybenzoyl)-4'-hydroxybenzophenone		diphenyl terephthalate	37
Tribenzoylphloroglucinol	30	phloroglucinol tribenzoate	26
4-Hydroxy-3-acetylbiphenyl		4-acetoxybiphenyl	9, 22
4-Hydroxy-4'-acetylbiphenyl	4	4-acetoxybiphenyl	22
4-Hydroxy-3-benzoylbiphenyl		4-benzoyloxybiphenyl	9, 20
4-Hydroxy-4'-benzoylbiphenyl	22	4-benzoyloxybiphenyl	9 21 27
5-Acetyl-2-hydroxybiphenyl		*o*-xenyl acetate	61
5-Propionyl-2-hydroxybiphenyl		*o*-xenyl propionate	61
5-*n*-Caproyl-2-hydroxybiphenyl		*o*-xenyl *n*-caproate	61
p-Hydroxyacetonaphthone	42-46 5	α-naphthyl acetate	2 40 12
o-Hydroxyacetonaphthone	16-18 61 50	α-naphthyl acetate	2 12 40
2,4-Diacetyl-1-naphthol	small 4	α-naphthyl acetate	40 12
1-Hydroxy-4-propionylnaphthalene	32-36 3	α-naphthyl butyrate	2 12
1-Hydroxy-2-propionylnaphthalene	20-23 55	α-naphthyl butyrate	2 12
2,4-Dibutyryl-α-naphthol	2	α-naphthyl butyrate	12
o-Propionyl-α-naphthol	54	α-naphthyl propionate	12
p-Propionyl-α-naphthol	6	α-naphthyl propionate	12
2,4-Dipropionyl-α-naphthol	2	α-naphthyl propionate	12
o-Valeryl-α-naphthol	40	α-naphthyl valerate	12
p-Valeryl-α-naphthol	2	α-naphthyl valerate	12
p-Hydroxynaphthyl benzyl ketone	34-37	α-naphthyl phenacetate	2
o-Hydroxynaphthyl benzyl ketone	14	α-naphthyl phenacetate	2
1-Acetyl-2-naphthol	40	β-naphthyl acetate	40
1-Acetyl-2-hydroxyfluorene or -fluorenone		2-acetylfluorene or -fluorenone	58
2,6-Dihydroxy-1,5-dibenzoylnaphthalene		naphthalene-2,6-dibenzoate	50
5-Bromo-2-hydroxyacetophenone		4-bromophenyl acetate	5
5-Bromo-2-hydroxypropiophenone		4-bromophenyl propionate	5
5-Bromo-2-hydroxybutyrophenone		4-bromophenyl butyrate	5
5-Bromo-2-hydroxyvalerophenone		4-bromophenyl valerate	5
5-Bromo-2-hydroxycaprophenone		*p*-bromophenyl caproate	5
2-Propionyl-4-chlorophenol		4-chlorophenyl propionate	11 40 51
2-Butyryl-4-chlorophenol		4-chlorophenyl butyrate	11, 49 51
4-Butyryl-2-chlorophenol		2-chlorophenyl butyrate	11, 40
o-Isobutyryl-*p*-chlorophenol		*p*-chlorophenyl isobutyrate	47
2-Valeryl-4-chlorophenol		4-chlorophenyl valerate	11 49
2-(α-Methyl butyryl)-4-chlorophenol		4-chlorophenyl-α-methyl butyrate	11, 49

Table 33—*(Continued)*

Ketone	% Yield	Ester	Ref.
2-Caproyl-4-chlorophenol		4-chlorophenyl caproate	11, 49
2-Heptoyl-4-chlorophenol		4-chlorophenyl heptanoate	11, 49
2-Caprylyl-4-chlorophenol		4-chlorophenyl caprylate	11, 49
3-Chloro-4-hydroxy-5-methylphenacyl chloride		3-chloro-*o*-tolyl chloroacetate	13
Acetyl-4-hydroxyphenylacetonitrile	75	4-acetoxybenzylcyanide	59
4-Bromo-2-acetylnaphthol		4-bromonaphthyl acetate	41
4-Chloro-2-acetyl-1-naphthol		4-chloro-α-naphthyl acetate	41
4-Chloro-2-propionyl-1-naphthol		4-chloro-α-naphthyl propionate	41
2,4-Dihydroxy-5-acetyldiphenylmethane		diphenylmethane-2,4-diacetate+2,4-dihydroxydiphenylmethane	54
2,4-Dihydroxy-5-propionyldiphenylmethane		diphenylmethane-2,4-dipropionate+2,4-dihydroxydiphenylmethane	54
2,4-Dihydroxy-5-butyryldiphenylmethane		diphenylmethane-2,4-dibutyrate+2,4-dihydroxydiphenylmethane	54
2,4-Dihydroxy-5-isovaleryldiphenylmethane		diphenylmethane-2,4-diisovalerate+2,4-dihydroxydiphenylmethane	54
2,4-Dihydroxy-5-acetyldiphenylethane		diphenylethane-2,4-diacetate+2,4-dihydroxydiphenylethane	54
2,4-Dihydroxy-5-butyryldiphenylethane		diphenylethane-2,4-dibutyrate+2,4-dihydroxydiphenylethane	54
2,4-Dihydroxy-5-isovaleryldiphenylethane		diphenylethane-2,4-diisovalerate+2,4-dihydroxydiphenylethane	54
2,4-Dihydroxy-5-acetyldiphenylpropane		diphenylpropane-2,4-diacetate+2,4-dihydroxydiphenylpropane	54
2,4-Dihydroxy-5-butyryldiphenylpropane		diphenylpropane-2,4-dibutyrate+2,4-dihydroxydiphenylpropane	54
2,4-Dihydroxy-5-isovaleryldiphenylethane		diphenylpropane-2,4,-diisovalerate+2,4-dihydroxydiphenylpropane	54
4-Methyl-6- or 8-acetylumbelliferone	15-20	4-methylumbelliferone acetate	52
8-*m*-Toluyl-4-methylumbelliferone		4-methylumbelliferone *m*-toluate	56
4-Methyl-8-benzoylumbelliferone	60-66	4-methylumbelliferone benzoate	18
8-*n*-Valeryl-4-methylumbelliferone		4-methylumbelliferone *n*-valerate	56
7-Hydroxy-8-acetyl-4'-methylcyclohexeno-(1',2',4,3)-coumarin		7-acetoxy-4'-methylcyclohexeno-(1',2',4,3)-coumarin	42
4-Methyl-7-hydroxy-8-acetylcoumarin		4-methyl-7-acetoxycoumarin	46, 55
4-Methyl-7-hydroxy-6-acetylcoumarin	4-5	4-methyl-7-acetoxycoumarin	46
6-Hydroxy-7-acetyl-2-isopropylcoumaran		6-acetoxy-2-isopropylcoumaran	44
5-Hydroxy-6-acetylflavone		5-acetoxyflavone	45
4-Methyl-7-hydroxy-8-propionylcoumarin		4-methyl-7-propionoxycoumarin	55
4-Methyl-7-hydroxy-8-butyrylcoumarin		4-methyl-7-butyroxycoumarin	55
7-Hydroxy-8(6)-benzoyl-2-methylchromone		7-benzoyloxy-2-methylchromone	57
7-Hydroxy-8-acetyl-2,3-dimethylchromone		7-acetoxy-2,3-dimethylchromone	57
7-Hydroxy-8-benzoyl-2,3-dimethylchromone		7-benzoyloxy-2,3-dimethylchromone	57
7-Hydroxy-8-acetyl-2-methylchromone		7-benzoyloxy-8-acetyl-2-methylchromone	57
7-Hydroxy-8-acetyl-2-methylchromone	50	7-acetoxy-8-acetyl-2-methylchromone	28
4-Butyryldiphenyl ether		*m*-tolyl butyrate and diphenyl ether	3

Table 33—*(Continued)*

Ketone	% Yield	Ester	Ref
4-Butyryl-*m*-cresol		*m*-tolyl butyrate and diphenyl ether	3
4-Acetyldiphenyl ether		*o*-tolyl acetate and diphenyl ether	3
4-Acetyl-*o*-cresol		*o*-tolyl acetate and diphenyl ether	3
4-Acetyldiphenyl ether		*p*-tolyl acetate and diphenyl ether	3
2-Acetyl-*p*-cresol		*p*-tolyl acetate and diphenyl ether	3
4-Benzoyldiphenyl ether		*o*-tolyl benzoate and diphenyl ether	3
4-Benzoyl-*o*-cresol		*o*-tolyl benzoate and diphenyl ether	3
o-Acetylphenol		phenyl acetate and *p*-tolyl chloroacetate	8 13
p-Acetylphenol		phenyl acetate and *p*-tolyl chloroacetate	13
2-Hydroxy-5-methylphenacyl-chloride		phenyl acetate and *p*-tolyl chloroacetate	13
3-Chloro-2-hydroxy-5-methylbenzo-phenone		3-chloro-*p*-tolyl acetate and *p*-tolyl benzoate	6
2-Hydroxy-5-methylacetophenone		2-chloro-*p*-tolyl acetate and *p*-tolyl benzoate	6
3-Chloro-2-hydroxy-5-methylaceto-phenone		2-chloro-*p*-tolyl acetate and *p*-tolyl benzoate	6
2-Hydroxy-5-methylbenzophenone		2-chloro-*p*-tolyl acetate and *p*-tolyl benzoate	6
2-Hydroxy-5-methylacetophenone		2-*m*-xylyl methyl ether and *p*-tolyl acetate	13
4-Hydroxy-3,5-dimethylacetophenone		2-*m*-xylyl methyl ether and *p*-tolyl acetate	13
Xylenol		2-*m*-xylyl acetate and *p*-tolyl benzoate	13
Cresol		2-*m*-xylyl acetate and *p*-tolyl benzoate	13
2-Hydroxy-5-methylacetophenone		2-*m*-xylyl acetate and *p*-tolyl benzoate	13
2-Hydroxy-5-methylbenzophenone		2-*m*-xylyl acetate and *p*-tolyl benzoate	13
4-Hydroxy-3,5-dimethylacetophenone		2-*m*-xylyl acetate and *p*-tolyl benzoate	13
2-Hydroxy-5-methylbenzophenone		2-hydroxymesitylene and *p*-tolyl benzoate	13
p-Cresol		2-acetoxymesitylene and *p*-tolyl chloro-acetate	13
2-Hydroxymesitylene		2-acetoxymesitylene and *p*-tolyl chloro-acetate	13
2-Hydroxy-3,4,5-trimethylaceto-phenone		2-acetoxymesitylene and *p*-tolyl chloro-acetate	13
2-Hydroxy-5-methylacetophenone		2-acetoxymesitylene and *p*-tolyl benzoate	13
2-Hydroxy-5-methylbenzophenone		2-acetoxymesitylene and *p*-tolyl benzoate	13
3-Chloro-2-hydroxy-5-methylaceto-phenone		2-acetoxymesitylene and 3-chloro-*p*-tolyl benzoate	13
3-Chloro-2-hydroxy-5-methylbenzo-phenone		2-acetoxymesitylene and 3-chloro-*p*-tolyl benzoate	13
2-Hydroxy-5-methylacetophenone		2,5-dimethyl-4-ethylphenyl chloroacetate and *p*-tolyl acetate	13

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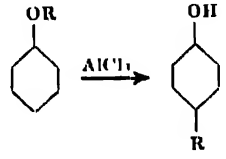
Rearrangement of Ethers

Rearrangement of alkyl phenyl ethers to substituted phenols is catalyzed by aluminum chloride:



A lesser amount of the *o*-alkyl phenol is obtained at the same time. The phenomenon was observed in 1892 by Hartmann and Gattermann [78] who converted isobutyl phenyl ether into *tert*-butylphenol by means of aluminum chloride.

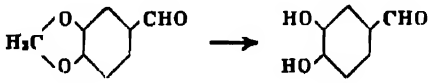
[78] C. Hartmann and L. Gattermann, *Ber.*, **25**, 3531-3534 (1892).

Chapter 16

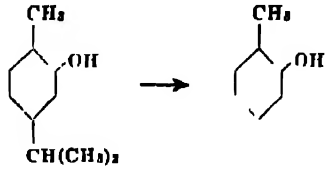
Effect of Aluminum Chloride on Aromatic Compounds

Anhydrous aluminum chloride has a pronounced effect on many pure aromatic compounds. This effect is particularly evident with aromatic hydrocarbons, and the course of such reactions is indicated in this chapter. Such reactions may include dehydrogenation, condensation, migration of alkyl side chains, isomerization, rearrangements, or simple cleavage. Whereas some of these types of reaction are dealt with in more detail in separate chapters, the general character and influence of such processes are shown here. Instances of the formation of polynuclear hydrocarbons by autocondensation of the aromatic hydrocarbons during Friedel and Crafts alkylation reactions are cited, since such reactions seem to demonstrate the tendency of these hydrocarbons to condense under a variety of conditions.

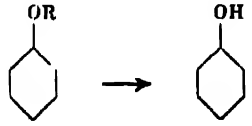
The cleavage of substituent groups from compounds other than hydrocarbons is also discussed in this chapter. For example, aluminum chloride can effect fission of a dioxymethylene ring in the conversion of piperonal to protocatechuic aldehyde:



Or it may convert carvacrol to *o*-cresol,



or convert phenol ethers to phenols, thus:



The cleavage of alkoxy- groups has been noted previously in Friedel and Crafts ketone synthesis and in reactions with phthalic anhydride. These reactions are discussed in more detail here to include not only

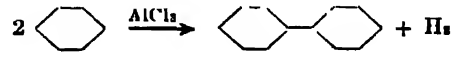
cleavage of phenol ethers, but also to demonstrate the applicability of this phenomenon to the preparation of hydroxy- ketones. Cleavage of groups from ketonic heterocyclic compounds, azo- compounds, *o*-aminophenol ethers, halogenated phenol ethers and alkoxyaryl aldehydes, and hydrolysis of esters are other phenomena which may occur in the presence of aluminum chloride.

Effect of Aluminum Chloride on Aromatic Hydrocarbons

The tendency of aluminum chloride to exert a disruptive effect on aromatic hydrocarbons has long been recognized as an irking factor in Friedel-Crafts reactions. Under varying conditions in the presence of aluminum chloride benzene has been shown to be converted to the following miscellany of products:*

toluene	*o*-diphenylcyclohexane
xylenes	phenylcyclohexane
ethylbenzene	naphthalene
cyclohexane	biphenyl
3-phenyl-1-methylcyclopentane	phenol and other phenols
	unsaturated oils and polymers

A variety of reactions is apparent. Obviously the action of aluminum chloride on benzene results in the loosening of hydrogen. It is uncertain whether biphenyl or phenylcyclohexane is the primary reaction product. Phenylcyclohexane has been shown to change probably into diphenylcyclohexane. This isomerizes to phenylmethylcyclopentane, which has been reported as the main reaction product.[1] If the reaction proceeds through primary formation of biphenyl,



the presence of cyclohexane may be ascribed to hydrogenation of the benzene by the evolved hydrogen. Cracking of the cycloparaffin would result in fragments that give alkyl benzenes upon reaction with benzene. Phenols are obviously secured through oxidation by air during treatment with aluminum chloride.

As is shown in Table 34 (p. 716), the extent of the change effected by aluminum chloride is of little significance in the case of benzene. As the complexity of the molecule increases, however, the disrupting action of the catalyst may become so great that it interferes with the normal course of Friedel-Crafts condensations. Rearrangement and cleavage of alkylated benzenes occur readily. It has been pointed out[2] that in the alkylation of toluene with isobutyl bromide in the presence of aluminum chloride the following products are secured besides butylated toluenes:

* See Table 34, p. 716.

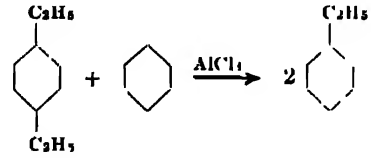
[1] E. Wertyporoch and H. Sagel, *Ber.*, 66, 1306-1312 (1933); *C. A.*, 28, 116.

[2] A. Bauer, *Ber.*, 24, 2832-2843 (1891); *ibid.*, 27, 1606-1609 (1894).

butylbenzene
ethylbenzene
butylethylbenzene
1,3-dimethyl-5-*tert*-butylbenzene
1,4-di-*tert*-butylbenzene

There is thus apparent a cleavage of toluene, with formation of benzene and xylene. This intramolecular migration of alkyl groups may proceed through formation of alkyl halide. Propyl chloride has been observed [3] as one of the products of the reaction of isopropylbenzene and isobutyl chloride in the presence of very small amounts of aluminum chloride at ordinary temperature. Other products included *tert*-butylbenzene and *p*-di-*tert*-butylbenzene. Methyl chloride has been reported as one of the products resulting from like treatment of *m*-xylene, or mesitylene.[4] Other investigators have noted evolution of paraffins during reaction of alkylated benzenes with aluminum chloride. Evolution of isobutane has been noted upon treatment of *tert*-butylbenzene [5] or *p*-*tert*-butyltoluene [6] with aluminum chloride. Like treatment of isopropylbenzene [7] and of cymene [8] has produced some propane. The fact that polymerization products are secured in most of these reactions may indicate, however, that the cleaved fragments are olefinic in nature, being converted to alkyl halide or paraffin through the hydrogen or hydrogen chloride evolved from side reactions.

The migration of alkyl groups which occurs when an alkylated aromatic hydrocarbon is heated with another aromatic hydrocarbon in the presence of aluminum chloride offers a new approach to the synthesis of alkylated hydrocarbons:



Alkylation by transfer of alkyl residues is more thoroughly discussed elsewhere.*

When polynuclear hydrocarbons are treated with lower alkyl halides and aluminum chloride, the dehydrogenating effect of aluminum chloride is stronger than its catalytic effect. The reaction

$$\xrightarrow{AlCl_3} RR + H_2$$

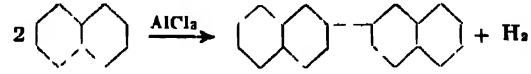
[3] E. Boedtker, *Bull. soc chim. (3)*, 35, 834 (1906).
[4] O. Jacobsen, *Ber.*, 18, 338-344 (1885)
[5] V. N. Ipatieff and H. Pines, *J. Am Chem. Soc.*, 59, 56-60 (1937)
[6] A. LaCourt, *Bull. soc. chim. Belg.*, 38, 1-20 (1929); *C. A.*, 23, 2341
[7] R. Hesse and A. Tohl, *Ann.*, 270, 155-171 (1892), *J. Chem Soc. Abs.*, 62, 1309 (1892); *ibid.*, *Ber.*, 24, 768-772 (1891).
[8] R. Anschutz and H. Immendorff, *Ber.*, 18, 657-662 (1885); *J. Chem. Soc. Abs.*, 48, 769 (1885) A. W. Schorger, *J. Am Chem Soc.*, 39, 2671-2679 (1917), *C. A.*, 12, 277.

* See page 690.

is more rapid than

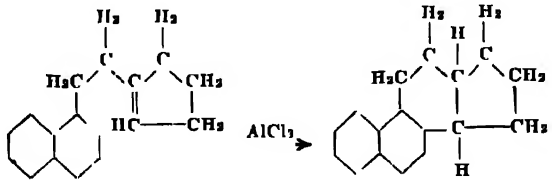
$$RH + AlkX \xrightarrow{AlCl_3} RAlk + HX$$

Thus, β,β'-binaphthyl is often reported as the major product in Friedel-Crafts reactions with naphthalene, two moles of naphthalene condensing according to the scheme:



Condensation of aromatic hydrocarbons under dehydrogenation has been repeatedly observed since the first announcement of the Friedel-Crafts reaction. That the dehydrogenating effect of aluminum chloride may be utilized for the synthesis of polynuclear hydrocarbons was indicated by Homer,[9] who secured picene derivatives from naphthalene, and by Scholl and his co-workers,[10] who obtained perylene as one of the products resulting from refluxing naphthalene with aluminum chloride at 180° for one hour. The production of polynuclear hydrocarbons through dehydrogenating condensation of aromatic hydrocarbons has been commercially advocated as a means of synthesizing fluorescent-imparting additives for lubricants. Scholl has extended the reaction to the auto-condensation of substituted aromatic hydrocarbons and to intramolecular ring closure of aroyl compounds. Scholl condensation with compounds other than aromatic hydrocarbons is treated separately.*

Aluminum chloride effects an isomerization of certain arylcycloalkene hydrocarbons which results in intramolecular ring closure [11]:



Since this isomerization proceeds through addition of an aryl nucleus at an olefinic bond, reactions of this type are more thoroughly discussed under reactions effected with unsaturated hydrocarbons.†

Inasmuch as the effect of aluminum chloride on aromatic hydrocarbons has been so often shown to result in the formation of a mixture of condensation, hydrogenation, rearrangement, and cleavage products, it has been thought expedient to avoid a classification of such reactions. The following table comprises a list of observations which have been

(*Text cont'd on p.* 723)

[9] A. Homer, *J. Chem. Soc.*, **97**, 1141-1154 (1910). *C. A.*, **5**, 1076; *Proc. Chem. Soc.*, **26**, 11-12 (1910).
[10] R. Scholl, C. Seer, and R. Weitzenbock, *Ber.*, **43**, 2202-2209 (1910). *J. Chem. Soc. Abs.*, **98** (I), 616 (1910).
* See page 649.
[11] J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 1098-1111 (1933).
† See page 486.

Table 34

Hydrocarbon	Reaction Conditions	Products	Ref
Benzene	20 weeks at 20°	phenylcyclohexane, biphenyl, *o*-diphenylcyclohexane, cyclohexane, phenylmethylcyclopentane	24
Benzene	24 hrs /125° with 10% $AlCl_3$+HCl and under pressure	biphenyl, ethylbenzene, unsaturated oil and polymers	25
Benzene	180-200° in a sealed tube	toluene, ethylbenzene; biphenyl, also phenols	7, 15
Benzene	24 hrs. at b p with 10% by wt. of $AlCl_3$	92% unchanged benzene, 1% phenols; 6 9% tar, and HCl	13
Benzene	$AlCl_3$+HCl, heated in sealed tube	3-phenyl-1-methylcyclopentane, b 230-232°; diphenylcyclohexane	21
Benzene	refluxing for 10-14 days at 100° with 25% $AlCl_3$	naphthalene, toluene, xylene, ethylbenzene, biphenyl, phenol	23
Benzene	$AlCl_3$ addition product of benzene, reaction with HCl gas	oil, b p 80-260° from which methylphenylcyclopentane, b 230-240° was secured; also diphenylcyclohexane	55
Benzene	nickel carbonyl and $AlCl_3$ at 100°	very small amount of aldehyde, anthracene, and nickel chloride	65
Benzene	*sym*-tetrabromoethane and $AlCl_3$	anthracene	73
Benzene	ethylidene chloride and $AlCl_3$	mesodimethylanthracenehydride and other products	17
Benzene	methylene chloride and $AlCl_3$	anthracene and other products	69
Toluene	3 hrs /110° 20% $AlCl_3$ in sealed tube	benzene, *p*- and *m*-xylene, and small amount of dimethylanthracene	1 26
Toluene	180-200° in a sealed tube	xylene, ethylbenzene, and tolyl also phenols	7 15
Toluene	24 hrs at b p with 10% by wt of $AlCl_3$	60% unchanged toluene, 15% benzene 3 5% xylenes, 1% phenols and 0 8% hexahydrotoluene	13
Toluene	3 hrs in a sealed tube with 30% $AlCl_3$	*m*- and *p*-xylene, dimethylanthracene; no *o*-xylene	17
Toluene	several hours with 9% $AlCl_3$ at b p	benzene, *m*- and *p*-xylene higher methylated benzenes, dimethylanthracene	27
Toluene	20% $AlCl_3$ heated under reflux with HCl	11 5% benzene, 80% C_7H_8 5 3% C_8H_{10}, b 136-143°	54
Toluene	20% $AlCl_3$ heated under reflux with nitrogen	8% benzene 90 5% C_7H_8 7% C_8H_{10}, b 136 143°	54
Toluene	20% $AlCl_3$ heated in distillation flasks with HCl	25 9% benzene 57 8% C_7H_8 6 8% C_8H_{10}	
Toluene	20% $AlCl_3$ heated in distillation flasks with nitrogen	14 2% benzene 83% C_7H_8 5 7% C_8H_{10}	
Toluene	20% $AlCl_3$ heated in distillation flasks with hydrogen	20 8% benzene 77% C_7H_8 8% C_8H_{10}	
Toluene	isobutyl bromide and $AlCl_3$	1,3-dimethyl-5-*tert*-butylbenzene 1,4,-di-*tert*-butylbenzene, di-*tert*-butylbenzene tributylbenzene, tributyltoluene	
Toluene	benzyl chloride and $AlCl_3$ or methylene chloride and $AlCl_3$	anthracene deriv, m p 231-232°, besides other compds	68 69
Toluene	isobutyl bromide and $AlCl_3$	butyltoluene, butylxylene, butylethylbenzene; dibutylbenzene, butylbenzene, ethylbenzene	62
Toluene	nickel carbonyl and $AlCl_3$ at 100°	very small amount of *p*-tolualdehyde and much 2,6-dimethylanthracene	65

Table 34—*(Continued)*

Hydrocarbon	Reaction Conditions	Products	Ref.
Toluene	chloroform and $AlCl_3$ in CS_2 soln.	dimethylanthracenes, besides other products	67, 72
Toluene	*sym*-tetrabromo- or tetrachloroethane and $AlCl_3$	dimethylanthracenes	17, 2 72
Toluene	ethylidene chloride	β,β-dimethylmesodimethylanthracenehydride	17
m-Xylene		toluene, benzene, mesitylene, pseudocumene, *p*-xylene, durene, and isodurene	1, 2
m-Xylene	5 hrs. at 100°, 10% $AlCl_3$ and HCl	benzene, toluene, mesitylene, and pseudocumene	18
m-Xylene	24 hrs. at b.p. with 10% by wt. of $AlCl_3$	5.6% benzene, 19% toluene, 30% unchanged xylene, phenols (appreciable amounts) some hexahydrotoluene	18
m-Xylene	boiled for 4 hrs. with 20% by wt. of $AlCl_3$	durene, mesitylene, pseudocumene, toluene, benzene, methyl chloride, *o*- and *p*-xylenes and *m*-xylene	16
m-Xylene	25-30% $AlCl_3$	toluene, *m*-xylene, *p*-xylene, mesitylene, pseudocumene, durene, and tetramethylanthracene, m.p. 290°	17
m-Xylene	mol. equiv. $AlCl_3$ for 15 min./94° with HCl	100% total xylenes recovered, consisting of *o*- 18% *m*- 72% *p*- 10%	64
m-Xylene	mol. equiv. $AlCl_3$ at 50° for 5 hrs.	96% total xylenes consisting of *o*- 14% *m*- 71% *p*- 15%	64
m-Xylene	same as above except HCl added	80% total xylenes consisting of *o*- 16% *m*- 67% *p*- 17%	64
m-Xylene	1 mole equiv. $AlCl_3$ at 50° for 0.5-75 hrs.	% total recovered hydrocarbons decreases from 92-59 with increasing time; % total xylenes in recovered hydrocarbons decreases from 100-72 with increasing time; % *o*-isomer in recovered xylenes is constant at about 16%; % *m*-isomer decreases from 77-65 with increasing time; % *p*-isomer increases from 3 to 19 with increasing time	64
m-Xylene	1-100 mol. equivalents of $AlCl_3$ at 50° with HCl for 48-50 hrs.	increase in molecular ratio of $AlCl_3$ increases rate of rearrangement and decomposition	64
m-Xylene	nickel carbonyl and $AlCl_3$ at 100°	small amount of 2,6-dimethylbenzaldehyde and much 2,4,6,8-tetramethylanthracene, m. 228-230°	65
m-Xylene	acetylene tetrabromide and $AlCl_3$	tetramethylanthracene and other products	17
m-Xylene	methylene chloride	an anthracene deriv., m. 162-163°	69
o- and *p*-Xylene	10% $AlCl_3$, 6 hrs./100° plus HCl	much *m*-xylene, benzene, mesitylene, and pseudocumene	18
o-Xylene	15 g of the xylene and 10 g of $AlCl_3$ at 55° for 10 min. with stream of HCl	81.6% *o*-xylene 0.0% *p*-xylene 18.7% *m*-xylene	11
p-Xylene	same as above	0.6% *o*-xylene 35.1% *p*-xylene 64.3% *m*-xylene	11
o-Xylene	1 mole equiv. $AlCl_3$ for 5 hrs./50° with HCl	94% total xylenes recovered, consisting of *o*- 40% *m*- 55% *p*- 5%	64

Table 34—*(Continued)*

Hydrocarbon	Reaction Conditions	Products	Ref.
o-Xylene	same as above except for 15 min./94°	84% total xylenes recovered, consisting of *o*- 88% *m*- 48% *p*- 16%	64
p-Xylene	mole equiv. $AlCl_3$ for 5 hrs at 50° with HCl	83% total xylenes recovered, consisting of *o*- 14% *m*- 76% *p*- 10%	64
p-Xylene	same as above except for 15 min./94°	90% total xylenes recovered, consisting of *o*- 16% *m*- 31% *p*- 53%	64
Xylene	heating at b.p. with moist $AlCl_3$	demethylated product	3
Xylene	HCl and $AlCl_3$	25-26% toluene	4
Xylene	4% $AlCl_3$ boiled 2 hours	86% of material b. below 140°	5
Xylene	refluxing	mesitylene and pseudocumene	6
Xylene	boiling for 3 hrs	fractions b. below and above xylene	9
Xylene	2% $AlCl_3$ at b.p. and atm. pressure	7% benzene 11% toluene	52
Xylene	heated in current of HCl with $AlCl_3$ at 100°	7.7% benzene 23.7% C_7H_8, 45.8% C_9H_{10}, and high boiling material	54
Xylene	heated in current of HCl with $AlCl_3$ at 120°	4.1% benzene, 16.3% C_7H_8, 37.0% C_9H_{10}, and high boiling material	54
Mesitylene	boiled with 10% by wt. of $AlCl_3$ and HCl for 4 hrs	durene, isodurene, pseudocumene (traces), *m*-xylene, toluene, benzene, methyl chloride and mainly unchanged mesitylene	16
Pseudocumene		toluene, benzene, *p*-xylene, pseudocumene, durene, isodurene, and mesitylene	1, 26
Pseudocumene	12% by wt. of $AlCl_3$ heated to boiling	pentamethylbenzene (traces), durene, isodurene, *m*- and *p*-xylene (mostly *m*-) toluene, and benzene	16
Pseudocumene		toluene, *m*- and *p*-xylene, mesitylene, durene, isodurene, and syrupy liquid	17
Durene		benzene	7
Tetramethylbenzene	10% $AlCl_3$	trimethylbenzene and xylene	7
Pentamethylbenzene	50% $AlCl_3$ for 14 days at 50-55°	durene, pentamethylbenzene, and hexamethylbenzene	16
Hexamethylbenzene	100-200° with 50% by wt. of $AlCl_3$	pentamethylbenzene, durene, isodurene, pseudocumene, mesitylene, *m*-xylene, toluene (very little), and benzene (very little)	16
Hexamethylbenzene		penta-, tetra-, tri-, and dimethyl benzenes and benzene	7, 15
Hexamethylbenzene		durene and other lower methylated benzenes	88
Ethylbenzene		benzene, much *p*-diethylbenzene, little *m*-diethylbenzene	1, 26
Ethylbenzene		no *o*-diethylbenzene	17
Ethylbenzene	2-10 hrs at 100-126° with $AlCl_3$ and HCl	benzene, *m*- and *p*-diethylbenzene, triethylbenzene	18
Isopropylbenzene	24 hrs. at b.p. with 10% by wt. of $AlCl_3$	1.5% benzene, 2.7% toluene 26.5% xylenes, 63.6% unchanged isopropylbenzene	13

Table 34—*(Continued)*

Hydrocarbon	Reaction Conditions	Products	Ref.
Isopropylbenzene	isobutyl chloride and very small amt AlCl at ordinary temp	*tert*-butylbenzene, *p*-di-*tert*-butylbutylbenzene, and propyl chloride	60
Isopropylbenzene	16 7% of $AlCl_3$ + HCl at 100° for 4 hrs	*m*- and *p*-diisopropylbenzene, benzene, propane, no toluene or xylenes	18
n-Propylbenzene	16 7% of $AlCl_3$ + HCl heating for 6 hrs at 100°	*m*- and *p*-dipropylbenzene, benzene, no toluene or xylenes	18, 29
n-Butylbenzene	16 7% of $AlCl_3$ + HCl heating for 6 hrs at 100°	*m*- and *p*-dibutylbenzene, *o*-, *m*-, and *p*-xylene pseudocumene mesitylene and benzene	18
sec-Butylbenzene	20% of $AlCl_3$ for 7 hrs 140-150°	liquid material, b p 120-210°	30
tert-Butylbenzene	27% $AlCl_3$ + HCl for 3 hrs 80°	isobutane gas, benzene, and higher boiling residues	31
tert Butylbenzene	isoamyl chloride and AlCl	isoamyl chloride recovered unchanged, *p*-di-*tert*-butylbenzene is obtained	60
p-Di-*n*-propylbenzene	33 3% $AlCl_3$ for 22 hrs at 100°	10% *p*-dipropylbenzene, 15% *m*-dipropylbenzene, 11% *n*-propylbenzene	34
m-Di-*n*-propyl benzene	33 3% $AlCl_3$ for 22 hrs at 100°	much unchanged material and a little *p*-di-*n*-propylbenzene	34
1 2,4-Tripropylbenzene	4 hrs at 100°	30% *m*-dipropylbenzene with a little *p*-isomer) 28% 1,3 5-tripropylbenzene 12% tetrapropylbenzene (probably)	34
Cymene	25% $AlCl_3$ at 175°	toluene, tar, and propane	1
Cymene	24 hrs at b p with 10% by wt of AlCl	0 9% benzene, 14 3% toluene, 7% xylenes 28 5% unchanged cymene, and 48 4% unidentified jelly-like mass	13
Cymene		mainly toluene	17
Cymene	20% $AlCl_3$ for 32 38 hrs at 60-98 heated in a current of an HCl or CO_2	benzene toluene *m*-xylene, 1-methyl-3,5-diisopropylbenzene, 2,3-dimethylbutane, and propane	32
Cymene	50% $AlCl_3$ for 4 hrs at room temp	benzene, toluene, xylene, unchanged cymene, 1,3,5-diisopropyltoluene, and a high boiling residue	33
p-tert Butyltoluene	50% AlCl for 10 hrs at room temp	toluene, dibutyltoluene, tributyltoluene, isobutane, unchanged *p-tert*-butyltoluene, and high boiling residue	33
Dibutylbenzene	room temp	tributylbenzene, butylbenzene, and an unidentified product	8
1 3-Dimethyl-4-isopropylbenzene	55°	largely to 1,3-dimethyl-5-isopropylbenzene	63
1,3-Dimethyl-4-*n*-propylbenzene	85-100°	mixture of 1 3,4- and 1,3,5-hydrocarbons, *m*-xylene and a dipropyl-1 3-dimethylbenzene	63
1,3-Dimethyl-4-*n*-butylbenzene		1,3-dimethyl-5-*sec*-butylbenzene	2
1 3-Dimethyl-4-*sec*-butylbenzene		1 3-dimethyl-5-*tert*-butylbenzene	2
1,3-Dimethyl-4-isobutylbenzene		mixture of hydrocarbons	2
1 3-Dimethyl-4-*tert*-butylbenzene		1 3-dimethyl-5-*tert*-butylbenzene	53
Naphthalene	refluxing for 1 hr at 180°	perylene	22
Naphthalene		benzene and hydrides of naphthalene	88
Naphthalene		isobinaphthyl and its isomerides	7
Naphthalene	90-150°	tetramethylnaphthalene, tetramethylpicene, β,β'-binaphthyl	40

Table 34—*(Continued)*

Hydrocarbon	Reaction Conditions	Products	Ref.
Naphthalene	4% $AlCl_3$ boiled for 1.5 hrs.	oily naphthalene, b. 210-225° and yellow, waxy mass	9
Naphthalene	100-150°	benzene, hydronaphthalenes, hydrogenated binaphthyls, β,β′-binaphthyl	14
Naphthalene	from 30 min. to 6 hrs.	no hydronaphthalene or hydronaphthyl; found: β,β′-binaphthyl, 1,4,5,8-tetramethylnaphthalene, b. 215-225°; $C_{22}H_{32}$ (an alkyl derivative of picene) and $C_{40}H_{32}$ (probably tetranaphthyl)	19, 20, 47, 48
Naphthalene		benzene, toluene, and other products	76
		compound having green fluorescence, apparently formed by union of 2 moles of benzanthrene	41
Naphthalene	methyl bromide or methyl chloride and HCl	8-10% methylnaphthalene and hydrocarbon, m.p. 173-174°, constitution not determined; no β,β′-binaphthyl	56
Naphthalene	methyl iodide and $AlCl_3$	no methylnaphthalenes; a hydrocarbon, b. 232°, picrate, m. 120°, is obtained	57
Naphthalene	methyl iodide and $AlCl_3$	5% methylnaphthalenes and β,β′-binaphthyl, m p. 180-181°	58
Naphthalene	amyl chloride or iodide and $AlCl_3$ at 120°	no amylnaphthalenes; ethyldimethylmethane and binaphthyl are obtained	57
Naphthalene	benzyl chloride and 4% $AlCl_3$ at 100-120°	benzylnaphthalenes and binaphthyl	57
Naphthalene	nickel carbonyl and $AlCl_3$ at 100°	no aldehyde; product contains C_6H_{12} (or $C_{28}H_{14}$-dinaphthanthracene?)	10, 47, 65
Naphthalene	isobutyl chloride and $AlCl_3$	two binaphthyls and tert-butyl naphthalene	59
Naphthalene	methylene chloride and $AlCl_3$	β,β′-binaphthyl and β-methylnaphthalene	70
Naphthalene	methylene chloride and AlCl	naphthalene and β,β′-binaphthyl	47
Naphthalene	*asym*-dichloroethane and $AlCl_3$	methylated naphthalenes and β,β′-binaphthyl	70
Naphthalene	*asym*-dichloroethane and $AlCl_3$	methylnaphthalenes, β,β′-binaphthyl, dinaphthylmethane, and substance, m.p. 252°	47
Naphthalene	ethylene bromide or chloride and $AlCl_3$	methyl- and ethylnaphthalenes and β,β′-binaphthyl	71
Naphthalene	same as above	above compds. and a crystalline product, m.p. 300°	57
Naphthalene	same as above, but distillation under reduced pressure	naphthalene, methylnaphthalenes, and picene, m.p. 359°; no β,β′-binaphthyl	47
Naphthalene	chloroform and $AlCl_3$	methylnaphthalenes, β,β′-binaphthyl, ethylnaphthalene, naphthalene	47
Naphthalene	tetrabromo- or tetrachloroethane and $AlCl_3$	$C_{28}H_{14}$, m.p. 267.5°, probably α,β,α′,β′-dinaphthanthracene	47
Acenaphthene	4% $AlCl_3$ boiled for 1.5 hrs.	fluorescent oil, b.p. 195-265°	9
meso-Dihydroanthracene	0.5 hr. at room temperature	72% anthracene	39
Anthracene	in nitrobenzene	no products isolated	39
Anthracene	4% $AlCl_3$ boiled for 1.5 hrs.	oil, b.p. 200-300°	9
Anthracene	3% $AlCl_3$ at 340°	hydroanthracenes, hydronaphthalenes, methylnaphthalene, carbon	37
Dihydrobenzanthrene or benzanthrene		green, fluorescent compound apparently formed by union of 2 moles of benzanthrene	41

Table 34—*(Continued)*

Hydrocarbon	Reaction Conditions	Products	Ref.
Phenanthrene	$AlCl_3+CS_2$ at 100°	yellow, amorphous substance, probably $(C_{14}H_{10})_x$	38
Phenanthrene	4% $AlCl_3$ boiled for 1.5 hrs.	yellowish green fluorescent oil	9
Phenanthrene	4.7% $AlCl_3$ at 340°	naphthalene, homologs of naphthalene, brown oil+HCl+hydrocarbon gas	37
Phenanthrene	in nitrobenzene	no products isolated	39
Phenanthrene		a condensation product, b_{10} above 310°, useful as pour-point depressant for lubricants	7
Pyrene	boiled for 10 min. with 5% $AlCl_3$	compound imparting fluorescence	42
Mixture of polynuclear aromatic hydrocarbons	45-55°	colors for dyeing lubricating oils	43
Chrysene		2,2'-bichrysenyl and then to dinaphthoperylene	44
Chrysene		2,3,10,11-dinaphthoperylene	91
Triphenylmethane		benzene	7
Triphenylmethane		diphenylmethane	88
Diphenylmethane	66% $AlCl_3$ for 17 hrs. at room temperature or at 85°	benzene and anthracene	39
Diphenylmethane		benzene and anthracene	10
sym-Diphenylethane		*meso*-dihydrodimethylanthracene	10
Stilbene	63.7% $AlCl_3$ in CS_2 8 hrs. at 100°	trimer of $C_{14}H_{12}$	38
Stilbene	$AlCl_3$ in CS_2	a polystilbene, m. 220°	89
Biphenyl		benzene	7
Biphenyl	250-300°	73.5% benzene 18.5% methylcyclopentane 4% cyclohexane 4% toluene	7 12
Isomeric binaphthyls	$AlCl_3$ alone or with KCl	perylene	28
2,2'-Binaphthyl	130-160°	perylene	49
1,1'-Binaphthyl	80% $AlCl_3$ for 1 hr. at 140°	perylene	22
1,1'-Binaphthyl		2,2'-binaphthyl	74
Hydrobinaphthyl		hydronaphthyls	14
3,4-Dihydro-1-phenethylphenanthrene or 3,4-Dihydro-1-(β-2'-tolylethyl)-phenanthrene	in CS_2 at 0° with equal amount by weight of $AlCl_3$	product which upon hydrogenation gave picene	92
Bicyclopentyl	170-290°	35% cyclohexane, 46% cyclopentane, 18.5% paraffin hydrocarbons	76
Bicyclohexyl	100° for 50 hrs.	*trans*-bicyclohexyl	85
Bicyclohexyl	160-290°	cyclohexanes, cyclopentane, and methane hydrocarbons	86
cis-9,9,3-Bicyclooctane	room temperature	isomerids, probably 1,2,3-bicyclooctane	83
Hydrindane	170-230° for 10 hrs.	23% hexamethylene hydrocarbons, 66.5% pentamethylene hydrocarbons, and 10.5% saturated aliphatic hydrocarbons	84
Tetralin	100°	benzene, octhracene, octanthrene	35
Tetralin	1.5-2% $AlCl_3$ for 6 hrs. at below 100°	benzene, tetralin, octahydrophenanthrene, octahydroanthracene	46
Tetralin	30-40° with 1.0-1.5% $AlCl_3$	*sym*-octahydrophenanthrene and *sym*-octahydroanthracene	36

Table 34—*(Continued)*

Hydrocarbon	Reaction Conditions	Products	Ref.
Tetralin	1-2% $AlCl_3$ at 50-70° for 10 hrs.	octahydrophenanthrene, benzene, octahydroanthracene, $C_{11}H_{16}$, 1-phenyl-4-(2-tetralyl)-butane, 2,2'-binaphthyl, 2,6'-ditetralyl	36
Tetralin	4% $AlCl_3$ at 70-80° for 8 hrs.	octahydrophenanthrene, dodecahydrotriphenylene, phenylene-bis- and tetralyloctanthrenylbutane	36
Tetralin	room temperature	benzene, octahydroanthracene, and -phenanthrene	45
Tetralin	10-30% $AlCl_3$ at 170-270°	50% of a distillate, b. 65-196°, containing 53% aromatic, 15% hexamethylene, 28.1% pentamethylene, and 3.9% paraffins	78
cis-Decahydronaphthalene		*trans*-isomeride and cleavage products	81, 87
Decahydronaphthalene	b.p.	hydrocarbons of composition $C_{10}H_{18}$, b. 157-250°	45
Decahydronaphthalene	130°	dimethyl-0,3,3-bicyclooctane, cyclohexane, methyl- and 1,3,5-trimethylcyclohexane	80
Octahydroanthracene	b.p.	tetradecahydroanthracene, tetralin, probably butadiene	50
Octahydroanthracene		50% of octahydrophenanthrene	36
Octahydroanthracene	b.p.	perhydroanthracene, decalin, polymethylene compounds, and probably tetralin and butadiene	51
Decahydroanthracene		16-24% aromatic compounds, 64-76% naphthenic compounds, and traces of aliphatic hydrocarbons	79
sym-Octahydrophenanthrene		*sym*-octahydroanthracene, dodecahydrophenalene	36

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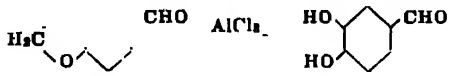
made concerning products secured by the action of aluminum chloride on aromatic hydrocarbons and hydrogenated polynuclear hydrocarbons. Illustrations of the production of polynuclear hydrocarbons by self-condensation of the aromatic component during Friedel-Crafts alkylation have been included, since the substances thus obtained are analogous to

those secured by the action of aluminum chloride on the aromatic hydrocarbon alone. Separate discussion has been made of alkylation by migration of alkyl groups,* isomerization of the alkyl group accompanying Friedel-Crafts reactions,† and intramolecular ring closure of arylcycloalkenes.‡

Cleavage of Compounds other than Hydrocarbons

At high temperatures, aluminum chloride effects fission of the dioxymethylene ring. Piperonal yields protocatechuic aldehyde:



Conversion is effected at 130-150° in benzene solution.[12] It may be advantageously conducted by using a chlorinated aliphatic hydrocarbon as solvent in the presence of at least two molar equivalents of aluminum chloride to one of piperonal.[13] When acetopiperone is treated with aluminum chloride in boiling chlorobenzene, acetopyrocatechol is secured. Similarly, piperonylic acid yields protocatechuic acid.[14]

Nitrodihydrosafrole is converted into 6-nitro-3,4-dihydroxy-1-isopropylbenzene by treatment with aluminum chloride in the presence of carbon disulfide [15]:

Oberlin has applied the reaction to a number of alkaloids containing a methylenedioxyl ring.[16]

According to Mosettig and Burger,[17] the scission of the methylenedioxyl group is efficiently effected in the presence of aluminum bromide, the use of this catalyst permitting lower reaction temperatures.

When acylation of aryl arsines is attempted by the Friedel-Crafts reaction, it results in decomposition with formation of arsenic trichloride. The liberated aromatic compound then unites with the acyl halide:

$$C_6H_5AsCl_2 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + AsCl_3$$

The reaction has been suggested as a means of identifying arsines.[18]

* See page 690.
† See page 94.
‡ See page 486.

[12] German P. 183,958 to C. Dreyfus; *C. Z.*, 1908 I, 1112.
[13] French P. 800,392 (1936) to Givaudan & Co.; *C. A.*, 30, 5248. U. S. P. 2,027,148 (1936) to M. S. Carpenter and E. C. Kuns (to Givaudan-Delawanna, Inc.); *C. A.*, 30, 1805.
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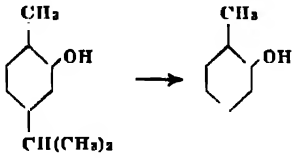
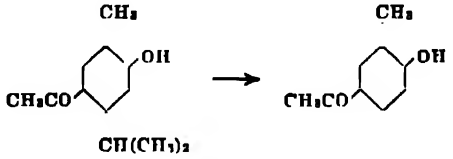
[17] E. Mosettig and A. Burger, *J. Am. Chem. Soc.*, 52, 2093-2094 (1930).
[18] M. S. Malinovskiĭ, *J. Gen. Chem. (U. S. S. R.)*, 5, 1355-1358 (1935); *C. A.*, 30, 3182.

Aluminum chloride in chlorobenzene, but not in nitrobenzene, at not over 50°, removes the isopropyl group from carvacrol and its acyl derivatives.[19] Carvacrol is transformed into *o*-cresol in 60 per cent yield:



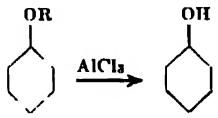
The isopropyl group is even more readily removed from thymol, a 92.5 per cent yield of *m*-cresol being obtained by like treatment. 5-Acetyl-2-hydroxy-1-methyl-4-isopropylbenzene gives 5-acetyl-2-hydroxytoluene in 53.3 per cent yield:



The isopropyl group is also removed from other acylated carvacrols. The isovaleryl group is similarly removed.

Cleavage of Phenol Ethers

When phenolic ethers are heated with an excess of aluminum chloride, cleavage occurs, with formation of the corresponding phenol:

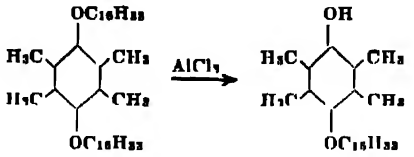


In 1892, Hartmann and Gattermann [20] investigated the effect of aluminum chloride on various phenol ethers, and found that cleavage of anisole, phenetole, *o*-nitrophenetole or -anisole, *o*-hydroxyanisole, *p*-acetylanisole or -phenetole, *p*-benzoylanisole and 4-acetylnaphthyl ethyl ether occurred by heating them at 100 to 200° for one-half to three hours with at least about an equivalent amount by weight of aluminum chloride. It was noted by these investigators that the cleavage of some of the substituted phenol ethers occurred more readily than that of anisole or phenetole.

Later investigations seem to show that the presence of a negative substituent in the phenol ether has a favorable effect on aluminum chloride-catalyzed cleavage of the ether, and that reaction proceeds most readily with phenol ethers in which the substituent is present in the ortho-

[19] H. John and P. Beetz, *J. prakt. Chem. (2)*, 149, 164-170 (1937); *C. Z.*, 1937 II, 4032.
[20] C. Hartmann and L. Gattermann, *Ber.*, 25, 3531-3534 (1892); *J. Chem. Soc. Abs.*, 64 (I), 152 (1893).

position. In effect, however, cleavage of any phenol ether may be brought about in the presence of an excess of aluminum chloride at elevated temperatures and with long reaction time. Thus, Fernholz and Finkelstein [21] used the method for preparing the monoacetyl ether of durohydroquinone:



The conversion was effected by refluxing the di-ether with 1.1 moles of aluminum chloride for eight hours in benzene suspension. When the procedure was repeated with 2 moles of aluminum chloride, cleavage of the alkoxy- was so complete that only durohydroquinone was secured.

Methoxy-substituted diphenyl ethers are demethylated on heating with aluminum chloride. If *o*-methoxydiphenyl ether in benzene solution is boiled with twice the amount by weight of aluminum chloride in a reflux apparatus, it yields *o*-hydroxydiphenyl ether; *o,o'*-dimethoxydiphenyl ether similarly yields *o,o'*-dihydroxyphenyl ether, but more aluminum chloride is needed for cleavage of the two methoxy- groups [22] *p*-Methoxy and *p,p'*-dimethoxybiphenyl likewise undergo demethylation to *p*-hydroxy and *p,p'*-dihydroxybiphenyl upon heating with aluminum chloride in benzene or xylene, respectively.[23]

Cleavage of alkoxy- occurs to some extent in any reaction involving the treatment of a phenol ether with more than an equivalent amount of aluminum chloride, the amount of dealkylation increasing with reaction time and temperature. Instances of this kind are especially prevalent in Friedel-Crafts ketone synthesis,* and in reactions with phthalic anhydride.† In both instances a molecular equivalent of catalyst is required for reaction to occur, and alkoxy- cleavage may only be avoided or minimized by working at low temperatures or by reducing the time of contact of the phenol ether with the catalyst.

Demethylation may occur during aluminum chloride-catalyzed halogenation of alkoxy- compounds. Thus, the action of sulfuryl chloride and aluminum chloride on *o*-nitroanisole leads to the formation of 4-chloro-2-nitrophenol and 4,6-dichloro-2-nitrophenol.[24]

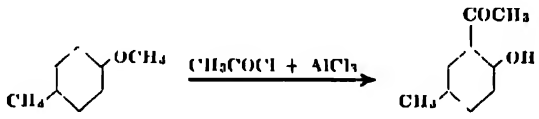
In the resumé of reactions involving alkoxy- cleavage which follows, no attempt has been made to review all cases in which dealkylation of phenol ethers occurs during aluminum chloride-catalyzed reactions. The fact that aluminum chloride cleaves phenol ethers has offered a ready

[21] E. Fernholz and J. Finkelstein, *J. Am. Chem. Soc.*, 60, 2402-2404 (1938); *Brit. Chem Abs*-B, 488 (1938).
[22] F. Ullmann and A. Stein, *Ber.*, 39, 622-625 (1906).
[23] M. Oesterlein, *Monatsh.*, 57, 31-44 (1931); *Brit. Chem. Abs*-A, 479 (1931).
* See page 302.
† See page 520.
[24] R. Gnehm and O. Knecht, *J. prakt. Chem. (2)*, 74, 92-111 (1906); *J. Chem. Soc. Abs.*, 90 (I), 825 (1906).

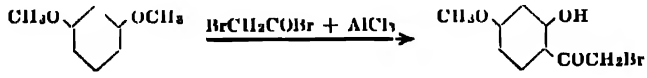
method for the preparation of difficultly obtainable phenolic compounds, and some representative conversions of phenol ethers to the corresponding phenols are listed. In spite of the fact that cleavage of alkoxy- is so readily catalyzed by aluminum chloride, no methodical study has been reported of the influence of substituents on the aluminum chloride catalyzed hydrolysis of ethers.

Preparation of Hydroxy- Ketones

Demethylation of phenol ethers has been frequently observed during Friedel-Crafts ketone synthesis.* The phenomenon has been observed particularly in reactions in which the entering acyl group takes the position *ortho-* to the alkoxy- group. Here alkoxy- cleavage occurs even under carefully controlled conditions. Thus, *p*-cresyl methyl ether yields 2-hydroxy-5-methylacetophenone upon treatment with acetyl chloride and aluminum chloride,[25]



and similar reaction with chloroacetyl chloride results in a 50-60 per cent yield of 2-hydroxy-5-methyl(chloroaceto)-phenone.[26] When dimethyl ethers are reacted with acyl halides in the presence of aluminum chloride, only the alkoxy- group *o-* to the acyl groups which has entered during the reaction is usually demethylated. Resorcinol dimethyl ether and bromoacetyl bromide yield ω-bromoresacetophenone monomethyl ether [27]:



Acyl ether	Product	Ref.
o-Methoxypropiophenone	o-hydroxypropiophenone	1
2,6-Dimethoxyacetophenone	2,6-dihydroxyacetophenone	2
2,4,6-Trimethoxyacetophenone	2-hydroxy-4,6-dimethoxyacetophenone	7, 6, 3
2,4,6-Trimethoxyacetophenone	hydroxymethoxyacetophenones	5
2,4,6-Trimethoxyacetophenone	2,4-dihydroxy-6-methoxyacetophenone	8
2,3,4,6-Tetramethoxyacetophenone	2-hydroxy-3,4,6-trimethoxyacetophenone	4

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3. W. A. Hutchins and T. S. Wheeler, *Current Sci.*, 6, 604-605 (1938); *C. A.*, 32, 8387.
4. S. Hattori, *Acta Phytochim.*, 5, 99-116 (1930); *Brit. Chem. Abs.*-A, 493 (1931).
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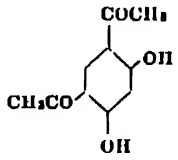
* See page 302.

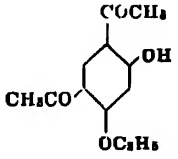
[25] A. J. Hill and L. E. Graf, *J. Am. Chem. Soc.*, 37, 1839-1846 (1915).
[26] K. v. Auwers, *Ann.*, 364, 147-182 (1909).
[27] J. Tambor and E. M. DuBois, *Ber.*, 51, 748-751 (1918).

Cleavage of the alkoxy- group rarely occurs in acylations involving the introduction of the acyl group in the *p*-position to the ether linkage; it occurs somewhat more readily in *meta*-substitution, but much more frequently in *ortho*-substitution. The preferential dealkylation of methoxy-*ortho* to the keto-group has offered a method for the synthesis of *ortho*-hydroxy- aromatic ketones, as shown in the conversions which have been effected by heating the indicated acyl ethers with aluminum chloride (see Table, p. 727).

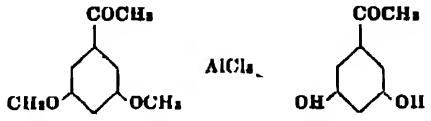
The cleavage of both methoxy- groups, as reported in the case of 2,6-dimethoxyacetophenone, is unusual. However, there has been much discussion of the products obtained from the reaction of resorcinol dialkyl ethers with acetyl chloride in the presence of aluminum chloride. For example, Claus and Huth [28] report the formation of a dihydroxyacetophenone (m.p. 178°) from resorcinol diethyl ether and acetyl chloride, and Eijkman and his co-workers [29] suggested that the product was 2,4-dihydroxy-1,5-diacetylbenzene (m.p. 183);



but Mauthner [30] was able to secure only one dealkylated product, 2-hydroxy-4-ethoxy-1,5-diacetylbenzene.



Another unusual case of alkoxy- cleavage is the formation of 3,5-dihydroxyacetophenone from the corresponding methoxy- compound:



The conversion was effected by heating 3 g of the ether with 10 g of aluminum chloride in 30 cc of chlorobenzene; 1.8 g of the dihydroxyketone was secured.[31] The fact that so great an excess of aluminum

[28] A. Claus and M. Huth, *J. prakt. Chem. (2)*, **53**, 39-42 (1896); *J. Chem. Soc. Abs.*, 70 (I), 227 (1896).
[29] J. F. Eijkman, F. Bergema and J. T. Henrard, *Chem. Weekblad*, **2**, 69-72, 79-93; *C. Z.*, 1905 I, 814-817.
[30] F. Mauthner, *J. prakt. Chem.*, **119**, 311-314 (1928); *C. Z.*, 1928 II, 1202.
[31] F. Mauthner, *J. prakt. Chem.*, **115**, 274-278 (1927); *C. A.*, **21**, 1808.

chloride was used and that the yield of the dihydroxy- ketone was only moderate, however, indicates the difficulty of hydrolyzing two methoxy- groups in *meta-* positions to the ketonic substituent.

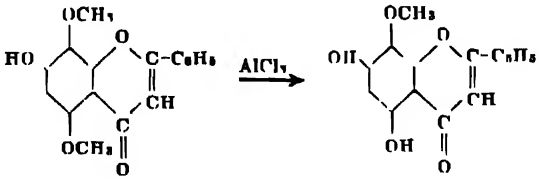
That cleavage of phenol ethers affords a method for the preparation of a large variety of hydroxy- ketones has been shown by von Auwers.[32] who prepared the following hydroxy- ketones by heating the corresponding ethers with aluminum chloride:

	m.p. (°C)
p-Hydroxyisovalerophenone	97–98
p-Hydroxypalmitophenone	78
3'-Nitro-4-hydroxybenzophenone	173
1-Nitro-4-hydroxybenzophenone	115
3-Methyl-6-hydroxypropiophenone	−2
3-Methyl-6-hydroxy-*n*-butyrophenone	34
3-Methyl-6-hydroxy-4'-nitrobenzophenone	142–143

In a subsequent study,[33] he noted that 4'-nitro-2-methoxybenzophenone was more readily cleaved than the 4'-nitro-4-methoxy isomer.

Alkoxy- Cleavage in Ketonic Heterocyclic Compounds

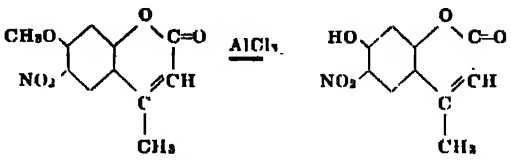
It has been found that when a polymethoxyflavone is subjected to the action of aluminum chloride, under mild conditions only the methoxy- group *ortho* to the carbonyl is demethylated.[34] Thus, treatment of 7-hydroxy-5,8-dimethoxyflavone with 0.75 mole of aluminum chloride yields 5,7-dihydroxy-8-methoxyflavone;[35] but with 1.5 mole of aluminum



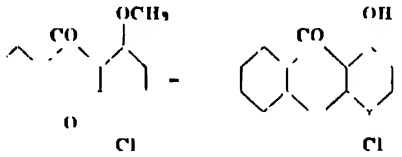
chloride demethylation of both alkoxy- groups occurs, with formation of 5,7,8-trihydroxyflavone.

Demethylation of 6-nitro-7-methoxy-4-methylcoumarin has been effected by heating 1.5 g of the compound with 4 g of aluminum chloride at temperatures gradually increasing to 150° for three hours.[36] Here the alkoxy- group is not adjacent to a carbonyl group, but it is *ortho* to the nitro- group, also a negative substituent:

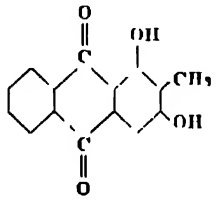
[32] K. v. Auwers, *Ber.*, **36**, 3890-3892 (1903).
[33] K. v. Auwers, *Ber.*, **36**, 3892-3902 (1903).
[34] K. Venkataraman and Bhadarwaj, *Current Sci.*, **2**, 50 (1934).
[35] R. C. Shah, C. R. Mehta, and T. S. Wheeler, *Current Sci.*, **6**, 503 (1938); *C. A.*, **32**, 5883; see W. Baker, N. C. Brown, and A. J. Scott, *J. Chem. Soc.* (1939) 1922-7 for similar cleavage of 5, 8-dimethoxyflavone, and K. Nakazawa, *J. Pharm Soc Japan*, **59**, 521-4 (in German, 196-8) (1939); *C. A.*, **34**, 1017, for alkoxy cleavage in 6-hydroxy-5-methoxyflavone and other flavones.
[36] D. Chakravarti and B. C. Banerjee, *J. Indian Chem. Soc.*, **14**, 37-38 (1937); *C. A.*, **31**, 5340.



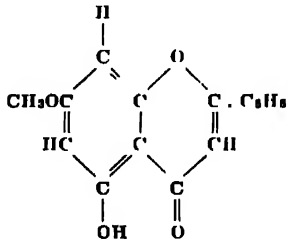
Aluminum chloride readily removes the methyl group from 4-chloro-1-methoxyxanthone [37]:



Aluminum chloride at 200° demethylates rubiadin methyl ether to rubiadin [38]:



Demethylation with aluminum chloride has also been extended to the chromone group.[39] Chrysin dimethyl ether in nitrobenzene solution with aluminum chloride is partially demethylated to tectochrysin,

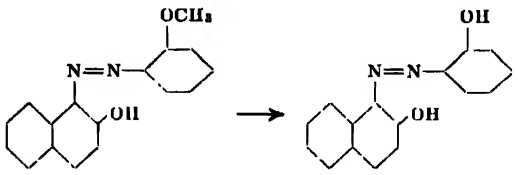


Alkoxy- Cleavage in Azo- Compounds

Ethers of hydroxyazo- compounds are readily hydrolyzed by treating them with aluminum chloride.[40] When *o*-anisylazo-*β*-naphthol is heated for a short time at 120-130° with 4 or 5 times its weight of aluminum

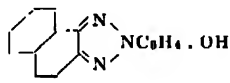
[37] A. Eckert and G. Endler, *J. prakt. Chem. (2)*, 104, 91-101 (1922); *J. Chem. Soc. Abs.*, 122 (I) 941 (1922).
[38] P. C. Mitter and H. Biswas, *J. Indian Chem. Soc.*, 7, 839-841 (1930); *Brit. Chem. Abs.*-A, 225 (1931).
[39] K. G. Gulati and K. Venkataraman, *J. Chem. Soc.*, 267-269 (1936).
[40] G. Charrier and P. Pellegrini, *Atti. acad. Sci. Torino*, 48, 978-981 (1913); *J. Chem. Soc. Abs.*, 104 (I), 1347 (1913).

chloride, and the reaction mixture boiled with dilute sodium hydroxide, the sodium salt of *o*-hydroxyphenylazo-*β*-naphthol is obtained, which can be converted to *o*-hydroxyphenylazo-*β*-naphthol; conversion of the ether to the hydroxy- compound thus proceeds:

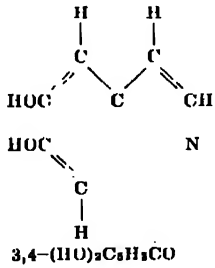


o-Phenetyl-, *p*-anisyl-, and *p*-phenetylazo-*β*-naphthol behave similarly.

N-Methoxy-substituted triazoles undergo similar cleavage; naphthalene-N-*p*-anisyltriazole yields the corresponding hydroxy- derivative.[41]



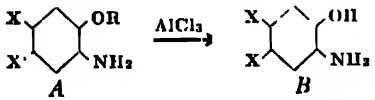
Oberlin [42] reports the use of aluminum chloride for the hydrolysis of alkoxy- groups in alkaloidal chemistry. Papaveraldine, having four alkoxy- groups, heated in intimate admixture with aluminum chloride yields papaveraldoline:



3,4-(HO)$_2$C$_6$H$_3$CO

Alkoxy- Cleavage in *o*-Amino-Phenol Ethers

o-Aminoalkoxy- phenols of the type *B* may be secured from aromatic *o*-aminoalkoxy- compounds of the type *A* by heating the latter with aluminum chloride in an organic solvent like benzene, cyclohexane, or aniline at temperatures up to 100°:

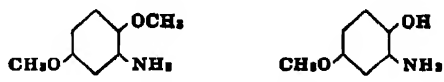


(one X is an alkoxy- group; the other X's are alkyl, alkoxy-, halogen, or hydrogen)

[41] Ferreri, *Gazz. chim. ital.*, 44 I, 632-641 (1914); *Atti. accad. sci. Torino*, 49, 497-507; *C. A.*, 8, 2686.

[42] M. Oberlin, *Arch. Pharm.*, 265, 256-273 (1927); *C. A.*, 21, 1988.

Thus, 2,5-dimethoxy-3-aminobenzene yields 4-methoxy-2-aminophenol[43]:



Other alkoxy *o*-aminophenols include the following:

4-ethoxy-2-aminophenol	2-amino-5-bromo-4-methoxyphenol
4,5-dimethoxy-2-aminophenol	5-methoxy-4-chloro-2-aminophenol
5-chloro-4-methoxy-2-aminophenol	5-methyl-4-methoxy-2-aminophenol

Alkoxy- Cleavage of Halogenated Phenol Ethers

Hayashi[44] noted that alkoxy- cleavage occurred during reaction of *o*- or *p*-chloroanisole with a number of acyl halides in presence of aluminum chloride in *sym*-tetrachloroethane at 120-130°. As noted below, the yield of hydroxy- ketone is greater when the entering acyl group goes *ortho* to the alkoxy-:

Ether	Acid Halides or Anhydride	Hydroxy- Product	% Yield
o-Chloroanisole	benzoyl chloride	3-chloro-4-hydroxybenzophenone	48.3
p-Chloroanisole	benzoyl chloride	5-chloro-2-hydroxybenzophenone	60.5
o-Chloroanisole	*o*-toluyl chloride	3-chloro-4-hydroxyphenyl *o*-tolyl ketone	25
p-Chloroanisole	*o*-toluyl chloride	5-chloro-2-hydroxyphenyl *o*-tolyl ketone	49.7
o-Chloroanisole	*m*-toluyl chloride	3-chloro-4-hydroxyphenyl *m*-tolyl ketone	14.7
p-Chloroanisole	*m*-toluyl chloride	5-chloro-2-hydroxyphenyl *m*-tolyl ketone	63 (the sole product)

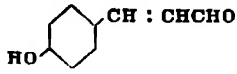
The conversion of fluorophenol ethers into fluorophenols is smoothly effected by means of aluminum chloride. When 27 g of *o*-fluoroanisole is treated with 70 g of aluminum chloride in 70 cc of benzene, and the mixture is heated on a water-bath for three hours, a 75 per cent yield of *o*-fluorophenol is obtained.[45] Similarly, the following fluorophenols in the indicated yields have been prepared from the corresponding methyl ethers:

Phenols	% Yield
p-Fluorophenol	68
m-Fluorophenol	95
2-Fluoro-4'-hydroxydiphenyl ether	53
2,3'-Difluoro-4'-hydroxydiphenyl ether	93

[43] Brit. P. 479,865 (1937) to I. G., French P. 824,127 (1938) to I. G.; *C. Z.*, 1938 I, 3837.
[44] M. Hayashi *J. prakt. Chem. (2)*, 123, 289-312 (1929); *Brit. Chem. Abs.*-A, 89 (1930).
[45] G. Schiemann, W. Winkelmüller, E. Bawler, E. Ley, G. Wiehage and M. Seyhan, *J. prakt. Chem.*, 143, 18-28 (1935); *C. A.*, 29, 7958. *Cf.* G. Schiemann and Kuhne, *Z. physik. Chem.*, 156A, 414 (1931); C. M. Suter, E. J. Lawson and P. G. Smith, *J. Am. Chem. Soc.*, 61, 161-165 (1939)

Alkoxy- Aryl Aldehydes

Of interest is the fact that demethylation of unsaturated aralkyl aldehydes may be brought about by treatment with aluminum chloride. *p*-Methoxycinnamaldehyde yields *p*-hydroxycinnamaldehyde [46]:



Hydrolysis of Esters

The hydrolysis of esters has been noted to occur during attempted Fries rearrangements. Thus, when a mixture of phenyl chloroacetate with 1.1 moles of aluminum chloride is allowed to stand for 24 hours, the sole products are the free phenol, monochloroacetic acid, and the unchanged ester.[47] The hydrolysis of the benzoate of 4-hydroxybiphenyl, together with some Fries rearrangement, has been noted upon treatment of the ester with aluminum chloride in tetrachloroethane.[48] In another instance of attempted rearrangement, 5-acetoxy-2-methyl-3-acetylchromone was converted not to the expected Fries migration product, but to 5-hydroxy-2-methyl-3-acetylchromone.[49]

Since the presence of a carboxy- group in the nucleus prevents Friedel-Crafts substitution, attempted acylation * of esters has often been reported to result not in the production of a substituted ester, but in the hydrolysis of the ester and possibly subsequent Friedel-Crafts reaction of the resulting phenol.

Norris and Klemka [50] have shown that ethyl 2,6-dichlorobenzoate is converted in 92 per cent yield into the acid and ethyl chloride when heated with aluminum chloride at 110°. Ethyl benzoate and ethyl acetate require higher temperatures for hydrolysis.[51]

[46] S. Takei, Y. Sakato and M. Ono, *Bull. Inst. Phys.-Chem. Research (Tokyo)* 17, 216-225 (1938); *C. A.*, 32, 7663.
[47] K. v. Auwers and W. Mauss, *Ann.*, 464, 293-311 (1928).
[48] D. Hey and E. R. B. Jackson, *J. Chem. Soc.*, 902-906 (1936).
[49] G. R. Kelgar and D. B. Limaye, *Rasāyanam*, 1, 50-54 (1936); *C. Z.*, 1937 I, 2598
* See page 364.
[50] J. F. Norris and A. J. Klemka, *J. Am. Chem. Soc.*, 62, 1432-1435 (1940).
[51] *cf.* J. F. Norris and P. Arthur, *J. Am. Chem. Soc.*, 62, 874-7 (1940).

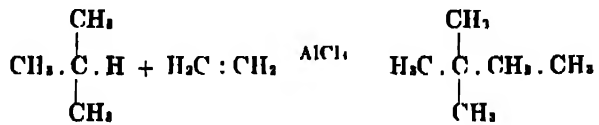
Chapter 17

Anhydrous Aluminum Chloride in Aliphatic Chemistry

The Friedel-Crafts reaction is generally considered as being limited to compounds of the aromatic series. Within the past decade, however, the reaction has been shown to be applicable to numerous condensations between two aliphatic components. In the older literature, only isolated instances of this type of condensation are mentioned.

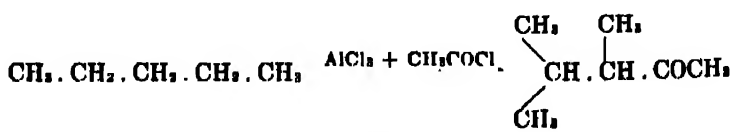
Generally speaking, aluminum chloride reactions in aliphatic chemistry require more careful observance of optimum reaction conditions than do comparable reactions in aromatic chemistry. Reactions involving paraffins call for higher temperatures and greater amounts of catalyst, and are complicated by the occurrence of concurrent cracking, dehydrogenation, and isomerization. Reactions in which an olefin is a constituent, on the other hand, often necessitate the use of low temperatures and less catalyst in order to avoid resinification. In both cases, reaction does not go as smoothly as in aromatic chemistry, and yield of definite product, is therefore not as great. Interest in the use of aluminum chloride in aliphatic chemistry is constantly advancing, however, because difficulties arising from lack of careful control of reaction conditions are being eliminated as techniques become improved; because of the great availability of aliphatic hydrocarbons from petroleum sources; and because of the insight into the mechanism of aromatic Friedel-Crafts reactions which recent work in analogous aliphatic reactions has afforded.

Although interaction of paraffins with alkyl halides in the presence of aluminum chloride has not been successful, alkylation of paraffins may be effected by reaction with olefins,

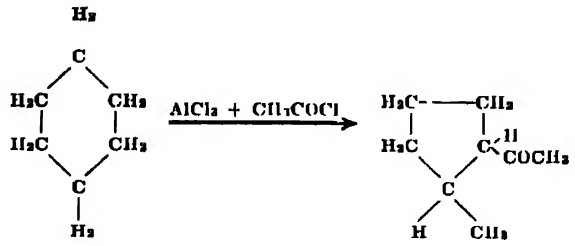


and cycloparaffins undergo analogous reaction. Alkylation may be effected with either straight-chain olefins or cycloölefins. Cycloparaffins may be added to cycloparaffins.

Paraffins or olefins have been condensed with acyl halides in the presence of aluminum chloride. Dialkyl ketones are secured:



Cycloparaffins also undergo isomerization during like treatment:



In the presence of a weakened catalyst, the corresponding unsaturated ketone is formed.

Olefins and cycloölefins yield unsaturated ketones when reacted with acyl halides in the presence of aluminum chloride. An intermediate formation of saturated β-chloroketones has been shown to occur:

$$CH_2 : CH_2 + CH_3COCl \xrightarrow{AlCl_3} \begin{matrix} /ClCH_2CH_2 \\ C{=}O \\ CH_3 \end{matrix} \xrightarrow{-HCl} \begin{matrix} CH_2 : CH \\ \diagdown \\ C{=}O \\ \diagup \\ CH_3 \end{matrix}$$

Acetylene yields an unsaturated β-chloroketone:

$$CH : CH \xrightarrow{CH_3COCl + AlCl_3} \begin{matrix} ClCH : CH \\ \diagdown \\ C{=}O \\ \diagup \\ CH_3 \end{matrix}$$

β-Halogenated acid chlorides may be prepared by addition of phosgene to olefins,

$$CH_2 : CHCH_3 + COCl_2 \longrightarrow \begin{matrix} CH_3 \\ | \\ CH_2Cl . CH . COCl \end{matrix}$$

and dialkyl ketones by addition of carbon monoxide to paraffins or cycloparaffins.

Acyl halides also condense with a wide miscellany of aliphatic compounds. With vinyl halides, saturated chloro-ketones are secured,

$$CH_2 : CHCl + RCOCl \xrightarrow{AlCl_3} R . CO . CHCl . CH_2Cl$$

which are easily dehydrohalogenated to β-chlorovinyl ketones,

$$R . CO . CH : CHCl$$

Treatment of carboxylic acid chlorides with carboxylic acids and aluminum chloride yields acid anhydrides. Dialkyl ethers and acid chlorides may react in the presence of aluminum chloride to yield esters. Con-

densations of acid halides with alcohols and with nitriles in the presence of aluminum chloride has been stated to give keto-esters and di-imides, respectively. Ketonic acids may be also obtained by Friedel-Crafts reaction of ketones with acid halides.

Aluminum chloride may be used as a catalyst in the production of esters from olefins and acids or for the formation of ethers from olefins and alcohols. It catalyzes the addition of olefinic oxides to halogen derivatives with formation of alcohols. It has been claimed to react as a dehydrating agent in production of ethers from alcohols, and as a hydrating agent in conversion of alcohols to ethers. It induces isomerization of paraffins and cyclization of paraffins or olefins. The widely studied polymerizing and cracking effect of aluminum chloride on aliphatic and cycloaliphatic hydrocarbons has been reserved for separate discussion.*

Aluminum chloride is an effective catalyst for promoting the addition of hydrogen halide or of halogen to olefins, and for halogenation of paraffins. It has been widely used in the preparation of polychloro- derivatives by addition of chloroparaffins to chlorinated ethylenes:

$$Cl_2C : CCl_2 + CHCl_3 \xrightarrow{AlCl_3} CHCl_2 . CCl_2 . CCl_3$$

Halogen exchange may be effected:

$$CHCl_3 + C_2H_5Br \xrightarrow{AlCl_3} C_2H_5Cl + CHCl_2Br$$

The disruptive effect of aluminum chloride, frequently decried, has been utilized in controlled dehydrohalogenation, as in the formation of perchloroethylene from pentachloroethane,

$$CHCl_2 . CCl_3 \qquad CCl_2 : CCl_2$$

or in the formation of difluorodichloromethane from two molecules of monofluorotrichloromethane:

$$2CCl_3F \xrightarrow{AlCl_3} CCl_2F_2 + CCl_4$$

The formation of aliphatic compounds of arsenic, nitrogen, phosphorus, or sulfur may be effected by treatment of the inorganic compound with an aliphatic hydrocarbon or derivative and aluminum chloride. The formation of metal alkyls through exchange reactions effected in the presence of Friedel-Crafts type catalysts is being investigated.

A more thorough discussion of aluminum chloride-catalyzed reactions in aliphatic chemistry follows:

Paraffins and Alkyl Halides

The possibility of alkylating paraffins by interaction with alkyl halides in the presence of aluminum chloride is open to question.

* See Chapter 18 for polymerization, and Chapter 19 for cracking.

Condensation of heptane with ethyl, propyl, isopropyl, or butyl chloride in the presence of aluminum chloride was attempted by Nenitzescu and Drăgan.[1] The heptane reacted energetically with aluminum chloride, with resulting isomerization, dehydrogenating condensation to higher hydrocarbons, and cracking to lower paraffins. A dehydrogenating cyclization also occurred. The hydrogen evolved reduced the alkyl halide present to the corresponding paraffins. The same processes were found to occur with *n*-hexane and with cyclohexane.[2] Attempts to bring about condensation of methylcyclopentane and dodecyl chloride by the Friedel-Crafts method have also been reported to be completely unsuccessful.[3]

The condensation of aliphatic saturated hydrocarbons with alkyl halides is covered in several patents[4] which preceded the investigations of Nenitzescu and his co-workers. Although in these patents hexane is claimed to be condensed with ethyl chloride in the presence of aluminum chloride, and at raised pressures, the nature of the reaction products, in view of the results obtained by the later investigators, is doubtful.

Recently the reaction of equal quantities by weight of hydrocarbon residues of high boiling point with chlorinated hydrocarbons of low boiling point, such as carbon tetrachloride or chlorinated naphtha, in the presence of aluminum chloride has been claimed to yield a normally gaseous mixture of light hydrocarbons which is composed principally of isoparaffins, and is substantially free of normal paraffins and olefins.[5] It has also been claimed that improved lubricating oils are obtained by treatment of lubricant stock with a small percentage of aluminum chloride and with a low-boiling halogenated hydrocarbon having not more than a single halogen atom attached to any one carbon atom and heating the mixture for one to two hours at 150° to 350° at atmospheric pressure.[6]

Reactions of hydrogenated polycyclic hydrocarbons are discussed elsewhere.*

Reaction of Paraffins with Olefins or Cycloparaffins

Although the alkylation of aromatic hydrocarbons with olefins has been known for a long time, it is only within the last few years that the alkylation of paraffins with olefins in the presence of Friedel-Crafts type catalysts has been known. In 1935 it was announced by Ipatieff and Grosse[7] that addition of paraffins to olefins takes place, under very mild conditions, in accordance with the reaction, for example, with isobutane and ethylene:

[1] C. D. Nenitzescu and A. Drăgan, *Ber.*, **66**, 1892-1900 (1933).
[2] C. D. Nenitzescu and C. I. Ionescu, *Ann.*, **491**, 189-210 (1931).
[3] H. Suida and A. Gemassmer, *Ber.*, **72**, 1168-1173 (1939); *C. A.*, **33**, 6807.
[4] British P. 327,411 (1928) to J. Y. Johnson (to I. G.); *Brit. Chem. Abs.*-B, 602 (1930); French P 660,739 (1929) to I. G., *C. A.*, **24**, 1866.
[5] U. S. P. 2,143,050 (1939) to H. G. Berger (to Socony-Vacuum Oil Co.); *C. A.*, **33**, 3119.
[6] U. S. P. 2,010,387 (1935) to E. Ayres and H. G. Smith (to Gulf Refining Co.).
* See Chapter V for alkylation of tetralin, acenaphthene, etc.
[7] V. N. Ipatieff and A. V. Grosse, *J. Am. Chem. Soc.*, **57**, 1616-1621 (1935).

With hydrogen chloride-activated aluminum chloride as catalyst the reaction has been shown to be a general one for both normal and isoparaffins with the exception of methane and ethane.[8] Alkylation of *n*-hexane was effected by passing pure ethylene into 147.7 g of nearly pure *n*-hexane with addition, from time to time, of a total of 25.1 g of aluminum chloride. As the absorption of ethylene slackened, a little dry hydrogen chloride was added to activate the reaction. After 15 hours, 61.3 g of ethylene had been absorbed, and two layers had been formed in the reaction mixture. The upper colorless layer, containing only traces of catalyst, consisted of saturated chlorine-free conversion products of 75 per cent of the initially present *n*-hexane. Paraffins from butane to dodecane have been similarly converted, the alkylating agents being ethylene, propylene, and the butenes. The reaction of isobutane with ethylene proceeds with great ease; on the average, one molecule of isobutane was found to condense with three molecules of ethylene.

The complexity of the reaction products indicates that the reaction does not involve only the addition of paraffin to olefin.

In most cases, further alkylation of the paraffin formed takes place. For instance with hexane the following occurs:

hexane + ethylene → octanes → decanes

With aluminum chloride as catalyst, the reaction is complicated by the following side reactions:

1. isomerization
2. autodestructive alkylation
3. polymerization of olefins
4. complex formation with aluminum chloride

In an investigation of the action of aluminum chloride on paraffins it has been found[9] that *n*-butane in the presence of aluminum chloride shows no appreciable change below 100°, but that at 175° during three or four hours it was converted to a large extent into propane, ethane, and methane and partly isomerized into isobutane. At this same temperature, *n*-hexane, *n*-heptane, and 2,2,4-trimethylpentane are completely decomposed. *n*-Hexane at its boiling point after three hours with aluminum chloride and hydrogen chloride is converted into higher and lower boiling olefins to the extent of 20-25 per cent. With *n*-heptane in the presence of aluminum chloride and a small amount of water, 35-40 per cent conversion occurred within three hours at its boiling point. 2,2,4-

[8] V. N. Ipatieff, A. V. Grosse, H. Pines, and V. I. Komarewsky, *J. Am. Chem. Soc.*, 58, 913-919 (1936).
[9] V. N. Ipatieff and A. V. Grosse, *Ind. Eng. Chem.*, 26, 461-464 (1934).

Trimethylpentane in the presence of aluminum chloride and hydrogen chloride is converted even at room temperature. At 25-30° in three to four hours about 90 per cent of it was changed into lower- and higher-boiling paraffin hydrocarbons.

The study showed that branched or long-chain paraffins are most susceptible to aluminum chloride and that hydrogen chloride, present either by direct addition or by formation from water and the catalyst or from the catalyst and the paraffin at high temperatures, is necessary.

"Autodestructive" alkylation, as described by Ipatieff and co-workers [10] consists in the splitting of a paraffin into a lower paraffin and an olefin, and the alkylation of another molecule of paraffin by the newly formed olefin with formation of a higher paraffin With isobutane and ethylene under pressure at room temperature in the presence of aluminum chloride the following products were obtained [11]:

Product	Vol % Yield
Isopentane	16.0
Hexanes	41.0
Heptanes	9 4
Octanes	12.3
Nonanes	6.5
Higher paraffins	14.8

About 80 per cent of the hexane fraction was 2,3-dimethylbutane. Autodestructive alkylation was probably responsible for the formation of isopentane. Assuming the preliminary formation of octane, the production of isopentane in the reaction may be according to the scheme:

$$(1)\quad C_8H_{18} \longrightarrow C_5H_{12} + C_3H_6$$
$$(2)\quad C_5H_{12} + C_3H_6 \longrightarrow C_{11}H_{24}$$
$$(3)\quad 2C_8H_{18} \longrightarrow C_5H_{12} + C_{11}H_{24}$$

The isopentane may also have been caused by the reaction of the cleaved propylene with isobutane to give heptane, which in turn was decomposed into isopentane and ethylene.

Ipatieff has advanced a probable mechanism for the alkylation of paraffins with olefins which involves the reaction of the paraffin with an aluminum chloride-olefin complex:

$$AlCl_3 + \tfrac{1}{2}C_2H_4 \longrightarrow ClCH_2CH_2AlCl_2$$
$$(CH_3)_2.CH + ClCH_2CH_2AlCl_2 \longrightarrow (CH_3)_2.C.CH_2CH_2AlCl_2 + HCl$$
$$(CH_3)_2.C.CH_2CH_2AlCl_2 + HCl \rightarrow (CH_3)_2.C.CH_2CH_3 + AlCl_3$$

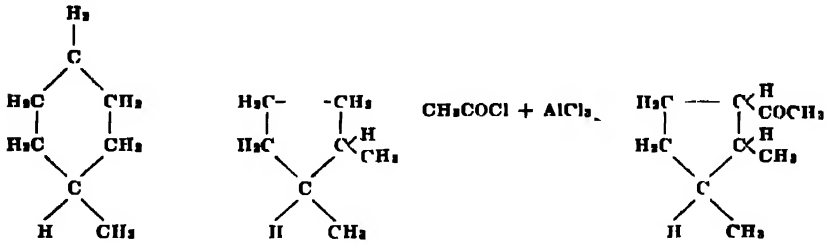
Although the reaction is general for *n*- and isoparaffins, the lower paraffins do not take part in the reaction. According to Ipatieff, the reason for this may be that a tertiary carbon atom is necessary for alkylation to occur.[11] Since methane, ethane, and propane do not possess tertiary carbon atoms, and cannot be isomerized to compounds which do, their

[10] V. N. Ipatieff, A. V. Grosse, H. Pines, and V. I Komarewsky, *J Am Chem Soc.*, **58**, 913-915 (1936).

[11] V. N. Ipatieff, *Oil Gas Journal*, *37* (46), 86-93 (1939).

resistance to alkylation may be accounted for on this basis. The presence of a tertiary carbon atom assures the presence of the labile hydrogen atom necessary for the addition, and thus may make possible the resulting condensation.

Noting that the presence of a tertiary carbon atom seems especially favorable in Friedel-Crafts condensations, Nenitzescu and his co-workers [12] had investigated the Friedel-Crafts acylation of methylcyclohexane, which has a tertiary carbon atom. Here only a 5-carbon ring ketone was obtained.



If tendency for reaction had been a specific property of a tertiary carbon atom, isomerization preliminary to condensation would not have occurred Contrary to the hypothesis expressed by Ipatieff, that the tertiary carbon atom is necessary for alkylation, the tertiary carbon atom appears not to be a prime requisite for acylation. The mechanism of Friedel-Crafts acylation of paraffins is pretty well shown by Nenitzescu and co-workers [13] to consist of a primary formation of olefins. The dehydrogenating action of aluminum chloride is well known. It is evident in the aluminum chloride-catalyzed Scholl reaction,* in the Anschütz anthracene synthesis,† and in dehydrogenation-hydrogenation phenomena observed by Nenitzescu and Isacescu [14] in the reduction of certain metal halides by the hydrogen resulting from the action of aluminum chloride on cyclohexane It is suggested by Nenitzescu [15] that probably in aliphatic alkylations there may be a primary dehydrogenation of paraffin to olefin. However, since it has been impossible to isolate the primary olefin in either Friedel-Crafts aliphatic acylations or alkylations, the views expressed are merely hypothetical.

The alkylation of paraffins by olefins in the presence of aluminum chloride has been covered by several patents. It is claimed that hydrocarbons, such as propane and butanes, are alkylated by olefinic hydrocarbons such as propylene and butenes at between −50° and +75° in the presence of aluminum chloride and hydrogen chloride. A pressure sufficient to keep the reacting compounds liquid is used.[16] A molecular

[12] C. D. Nenitzescu, E. Cioranescu, and I. P. Cantuniari, *Ber.*, **70**, 277-282 (1937).
[13] C. D. Nenitzescu and I. Chicos, *Ber.*, **68**, 1584-1587 (1935).
* See page 649.
† See page 111.
[14] C. D. Nenitzescu and D. A. Isacescu, *Ber.*, **67**, 1391-1398 (1934).
[15] C. D. Nenitzescu, *Angew. Chemie*, **52**, 231-236 (1939).
[16] French P. 833,862 (1938) to Universal Oil Products Co.; *C. A.*, **32**, 5618.

excess of the paraffin relative to the olefin is maintained during the reaction.[17] Thus, *n*-butane and propene in weight ratio of 3 to 1 are forced into an autoclave containing 1 part by weight of aluminum chloride and 0.1 part hydrogen chloride at 65° and 150-200 lb./sq. in. of pressure. Propane, the alkylation of which has not been effected under ordinary conditions,[18] may be alkylated in the presence of aluminum chloride and under pressure. In this case, a 3 to 1 mixture of propane and olefin is forced into a vessel containing 2 parts aluminum chloride and 0.2 part hydrogen chloride at 70°C and 600 lb./sq. in. of pressure.

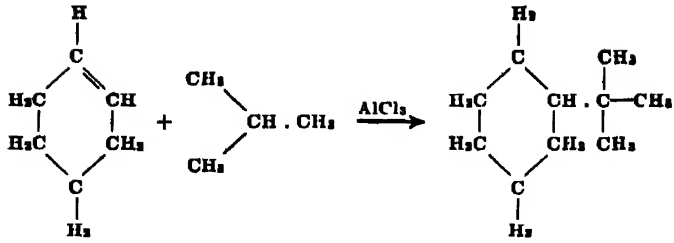
Temperatures of below 0° are used in the production of hydrocarbons of gasoline boiling point range by the alkylation of isobutane with olefins.[19] Small amounts of hydrogen chloride may also be used in the reaction.[20] In an example,[21] granular anhydrous aluminum chloride was placed in a reaction vessel which was cooled to a temperature of −30°. To activate this material, a total of 2 parts by weight of an equal mixture of isobutane and isobutene was contacted with it. Leaving the activating hydrocarbon mixture in place, the liquid mixture of isobutane and propylene was contacted in such a way that the charge entered below the surface of the hydrocarbon liquid containing the suspended aluminum chloride, while reaction products were siphoned from the reaction vessel at a sufficiently high level to avoid removal of the catalyst particles. The charge consisted of approximately 77 per cent of isobutane and 23 per cent of propylene, calculated on a gas basis, and a steady feed of a small amount of hydrogen chloride was maintained during the run. Operating under these conditions, 3250 volumes of isobutane-propylene mixture produced 650 volumes of liquids boiling within the ordinary range of commercial gasoline or up to approximately 225°C. 90 per cent of the total liquid products boiled below 220°C.

An improved process for the production of gasoline boiling-range hydrocarbons comprises the alkylation of isobutane with *n*-butenes in the substantial absence of isobutene, and in the presence of aluminum chloride at temperatures of 0° or below.[22]

The alkylation of isobutane for the production of motor fuel is of commercial significance because of the high antiknock value of the resulting product, and because the olefinic constituent may be a mixture of olefins with one another or with inert gases, for example, petroleum cracking gases.[23]

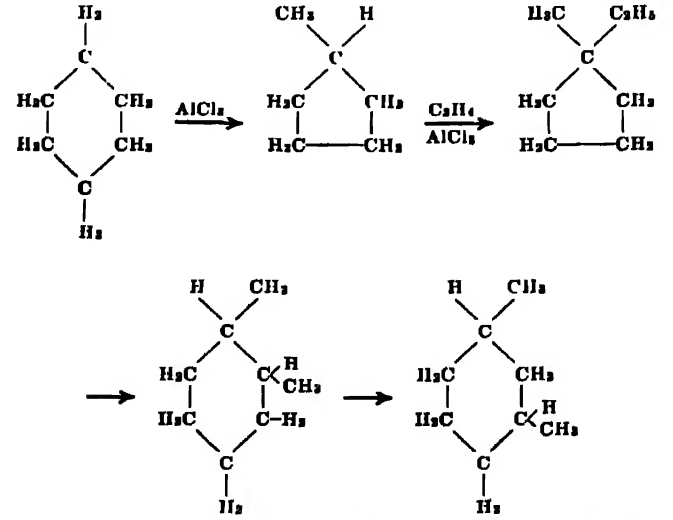
It has been reported[24] that cyclohexene readily reacts with paraffins in the presence of aluminum chloride at room temperature. The scheme of the main reactions which take place is described as follows:

[17] British P. 497,782 (1938) to Universal Oil Products Co.; *Chemical Trade Journal*, 270, March 17, 1939.
[18] V. N. Ipatieff, *Oil Gas Journal*, 37 (46), 86-92 (1939).
[19] U. S. P. 2,112,846 (1938) to V. N. Ipatieff and H. Pines (to Universal Oil Products Co.).
[20] French P. 833,598 (1938) to Universal Oil Products Co., *C. A.*, 32, 5618; British P. 496,273 (1938) to Universal Oil Products Co.; *J. Inst. Petr.*, 25, 59A (1939)
[21] U. S. P. 2,112,847 to V. N. Ipatieff and H. Pines (to Universal Oil Products Co.).
[22] U. S. P. 2,170,306 (1939) to V. N. Ipatieff and H. Pines (to Universal Oil Products Co.).
[23] Brit. P. 496,273 (1938) to Universal Oil Products, *C. A.*, 33, 3136; for a study of the use of double chloride of aluminum and alkali metals, *e.g.*, $NaAlCl_4$, in this reaction see F. H. Blunck and D. R. Carmody, *Ind. Eng. Chem.*, 32, 328-330 (1940).
[24] H. Pines, Paper presented at April, 1938, meeting of American Chemical Society, Dallas, Texas.



The *tert*-butylcyclohexane, which is probably formed first, undergoes isomerization into dimethylethylcyclohexane. Another side reaction consists of the condensation of the alkylated cyclohexane with the cyclohexene to yield alkylated dicyclo- compounds. Hydrogenation of some cyclohexene also occurred. The hydrogen necessary for this may have been supplied by the dehydrogenation occurring during the condensation of two molecules of alkylated cyclohexane, and by the evolution of hydrogen occurring during formation of compounds of the composition C_nH_{2n-2} which were found in the catalyst layer.

Saturated alicyclic compounds, for example, cyclohexane, have been alkylated by olefins in the presence of aluminum chloride.[25] The reaction is similar to that of paraffins with olefins. The main products of the alkylation of cyclohexane with ethylene are not ethylated cyclohexanes, as would be expected from the fact that benzene reacts with ethylene to give ethylbenzenes, but isomerization products of ethylated cyclohexanes, namely dimethyl- and tetramethylcyclohexanes. Ipatieff[26] suggests the following scheme of reaction:



[25] V. N. Ipatieff, V. I Komarewsky, and A. V Grosse, *J. Am. Chem. Soc.*, **57**, 1722-1724 (1935).
[26] V. N. Ipatieff, *Oil Gas Journal*, **37**, 86-93 (1939).

The reaction thus probably involves the preliminary isomerization of cyclohexane to methylcyclopentane, introduction of the ethylene into the methylcyclopentane molecule, and a shifting of the methyl groups with derangement of the cyclopentane structure. Each step of the foregoing scheme has been shown to take place with pure compounds.

Cyclopentane cannot be alkylated with ethylene in the presence of aluminum chloride. This fact lends some weight to the hypothesis that a tertiary carbon atom is necessary for alkylation to occur, since aluminum chloride can have no isomerizing effect on cyclopentane to form a tertiary carbon atom. Another point in favor of this hypothesis is the fact that boron fluoride, which is known not to isomerize cyclohexane, does not catalyze alkylation of cyclohexane with ethylene. This may be due to the fact that preliminary isomerization to a compound containing a tertiary carbon atom is necessary for alkylation to occur. Methylcyclohexane and methylcyclopentane, which do possess tertiary carbon atoms, are readily alkylated by ethylene in the presence of aluminum chloride or boron fluoride.

The alkylation of cyclohexane with ethylene is of sufficient interest to warrant rather detailed description. Cyclohexane (295 g) was heated on a water-bath to 50-60°, and then saturated, with vigorous stirring, with ethylene and hydrogen chloride. Upon addition of 30 g of aluminum chloride, the absorption of ethylene began. Ethylene was passed into the reaction mixture at the rate of 4-5 liters per hour for 13 hours. Every hour hydrogen chloride was introduced for one-half hour. Additional aluminum chloride was added twice during the experiment, 7.5 g being introduced each time. The reaction product consisted of 326 g of clear liquid layer and 67 g of a pasty catalyst mass. The liquid layer was separated into a fraction b. 70-90° and another fraction b. 90° and higher. The fraction b. 70-90°, weighing 155 g, consisted of unreacted cyclohexane and its isomer, methylcyclopentane. The fraction b. 90° and higher, weighing 162 g, consisted of the alkylation products. *m*-Dimethylcyclohexane and tetramethylcyclohexane were found to be present in this fraction.

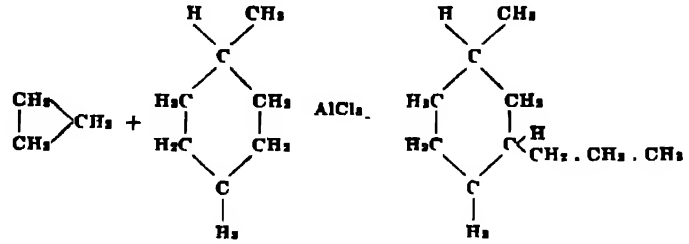
From the catalyst layer there was isolated an interesting by-product, hexaethylbenzene. This indicates an intermediate formation of hexaethylcyclohexane. Ethane was also one of the by-products; the hydrogen necessary for the conversion of ethylene into ethane may have resulted from the dehydrogenation of hexaethylcyclohexane to hexaethylbenzene.

Alkyl derivatives of hydrocarbons, useful as fuels and lubricants are claimed as products of the reaction of paraffins or naphthenes with cycloparaffins containing less than 5 carbon atoms in the ring.[27] Aluminum chloride is used as catalyst, and the reaction is performed at −40° to 15° in the presence of hydrogen chloride. In this way cyclopropane has been reacted with methylcyclohexane at about −10° to give 1-methyl-3-propylcyclohexane (b.p. 166.5-168.5°/745 mm) in 40 per cent yield and

[27] British P. 498,860 to A. L. Mond (to Universal Oil Products Co.); *C. A.*, 33, 3809; U. S. P. 2,182,587 (1940) to A. V. Grosse (to Universal Oil Products Co.); *C. A.*, 35, 1995.

a dipropylmethylcyclohexane in a 20 per cent yield. At 15°, the same products are obtained in 50 and 25 per cent yields respectively, and hexapropylbenzene is also obtained in a 5 per cent yield.

There is observed here the decycloalkylation reported by Grosse and Ipatieff [28] in the reaction of cycloparaffins with aromatic hydrocarbons. The smoothness of the reaction depends, of course, on the stability of the cycloparaffin; because of the instability of the cyclopropane and cyclobutane rings the reaction proceeds with easy decyclization of the ring and simultaneous alkylation of the more stable hydrocarbon component present. With cyclopropane and methylcyclohexane it probably occurs:



The production of hexapropylbenzene at the higher temperature indicates dehydrogenation of some of the cyclohexane under the influence of aluminum chloride at this temperature.

Synthetic lubricants have been secured by condensation of hydroaromatic hydrocarbons with olefins and aluminum chloride at 180-200 in a rotating Bergius autoclave. Decalin, hexahydropseudocumene, and hexahydromesitylene condense smoothly with amylene under these conditions.[29]

Reaction of Paraffins with Acyl Halides

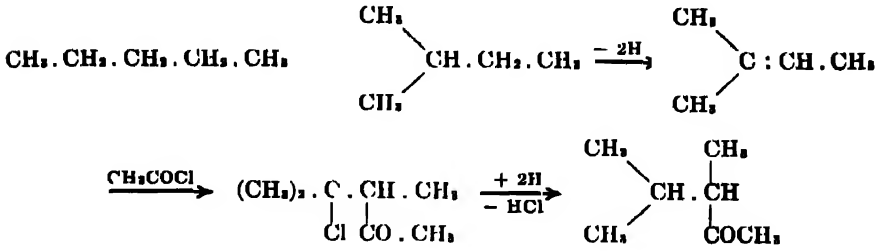
Butane, pentane, and hexane have been shown to react with acyl halides in the presence of aluminum chloride to give low yields of ketones.

In 1936 Hopff and his co-workers [30] reported that if acetyl chloride is reacted with *n*-butane and aluminum chloride in the cold, the reaction product is acetylacetone, doubtless resulting from the self-condensation of the acetyl chloride. If the reaction is allowed to proceed at 50-60°, however, methyl isobutyl ketone is one of the reaction products. Upon heating 700 g of *n*-butane, 500 g of aluminum chloride, and 320 g of acetyl chloride for fifteen hours at 60°, there was obtained 70 g of a fraction b. 80-135° from which methyl isobutyl ketone (b. 117-118°) was isolated. Isobutane reacts under similar conditions to yield the same product.

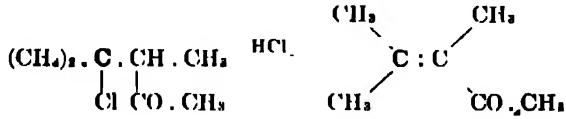
In a preliminary investigation Hopff [31] reported that reaction of *n*-pentane with acetyl chloride and aluminum chloride gave 2-acetyl-

[28] A. V. Grosse and V. N. Ipatieff, *J. Organic Chemistry*, 2, 447-458 (1937).
[29] A. D. Petrow, *Chimija tverdogo Topliwa*, 5, 632-641; *C. Z.*, 1936 I, 251.
[30] H. Hopff, C. D. Nenitzescu, D. A. Isacescu, and I. P. Cantuniari, *Ber.*, 69, 2244-2251 (1936)
[31] H. Hopff, *Ber.*, 64, 2738-2743 (1931); *C. A.*, 26, 1236.

pentane. Subsequently Nenitzescu and Chicos [32] showed that the reaction product was in reality methyl isopropyl acetone. The formation of this ketone was attributed by these investigators to occur according to the reaction scheme:

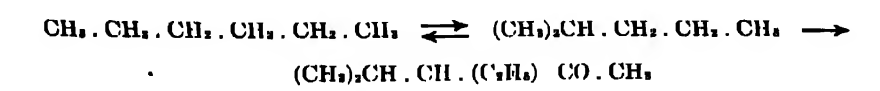


The formation of this product depends upon the presence of sufficient hydrogen to effect simultaneous hydrogenation and dehydrohalogenation, the hydrogen being supplied by aluminum chloride-induced condensations. If the catalyst is not present in sufficient amounts, or if it is weakened in any way, such hydrogen is not available and the last step of the reaction becomes



For this reason the unsaturated ketone, α-methyl-α-isopropylidene acetone, is often secured as a by-product in the reaction.

n-Hexane and acetyl chloride react similarly.[33] Here there is also first an isomerization to 2-methylpentane, with subsequent acetylation:



In this case, too, there is obtained as by-product an unsaturated ketone. This has been proved to be α-ethyl-α-isopropylideneacetone.[32]

The evolution of hydrogen during the action of aluminum chloride on saturated hydrocarbons is further substantiated in that the action of aluminum chloride on saturated hydrocarbons in the presence of arsenic or phosphorus trichloride has been shown by Nenitzescu and Isaccscu [34] to result in reduction of the salts to elemental arsenic or phosphorus.

According to other investigators, however, *n*-paraffinic hydrocarbons cannot be acetylated by the Friedel-Crafts reaction. Zelinsky and Leder-Packendorff [35] have attempted the acetylation of a petroleum distillate

[32] C. D. Nenitzescu and I. Chicos, *Ber.*, **68**, 1584-1587 (1935); *C. A.*, **29**, 7279.
[33] C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, **65**, 1449-1453 (1932); C. D. Nenitzescu and A. Dragan, *Ber.*, **66**, 1892-1900 (1933).
[34] C. D. Nenitzescu and D. A. Isaccscu, *Ber.*, **67**, 1391-1394 (1934).
[35] N. D. Zelinsky and L. Leder-Packendorff, *Ann.*, **518**, 260-274 (1935).

which had been freed of aromatics and cyclohexanes, and which contained only paraffins and cyclopentanes. The only ketones obtained were 5-membered ring compounds. Under the conditions used by these experimenters, the paraffins did not react. Similar treatment of 2-methylpentane and *n*-hexane also did not result in the formation of ketones. These contradictory reports may be ascribed only to differences in experimental conditions. According to Nenitzescu and Cantuniari [33] the acetylation of paraffins proceeds very slowly, being accompanied by simultaneous isomerization, dehydrogenating condensations to higher hydrocarbons, and dehydrogenating cyclization of the paraffins. The yield of ketone is consequently very low. In reacting 1000 cc of *n*-hexane with 300 g of freshly sublimed aluminum chloride and 150 g of acetyl chloride, they secured only 17 g of the fraction b. 155-160°, from which the saturated ketone, α-ethyl-α-isopropylacetone was secured through conversion into the semicarbazone. At the same time there was obtained 31 g of the fraction b. 78-89°, from which the unsaturated ketone, α-ethyl-α-isopropylideneacetone was isolated.

The condensation of paraffinic hydrocarbons with acyl halides in the presence of aluminum chloride and under high pressure is covered by several patents.[36] Reaction of hexane with acetyl chloride is reported to yield octanone, together with other polymethylene ketones.

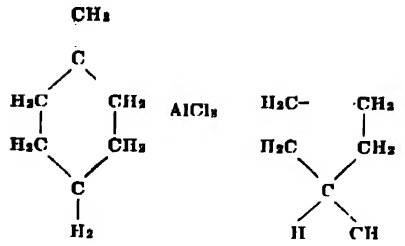
Carbamyl chloride or its alkyl derivatives has been claimed [37] to react with paraffins of more than 3 carbon atoms at 100-200° in the presence of aluminum chloride to yield carboxylic acid amides. Treatment of *n*-pentane with a molecular compound of aluminum chloride and carbamic acid chloride and subsequent heating for twelve hours at 130-140 in a closed vessel yields a caproic acid amide:

$$C_5H_{12} + ClCONH_2 \longrightarrow C_5H_{11}CONH_2 + HCl$$

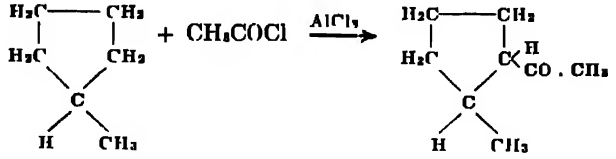
Reaction of Cycloparaffins with Acyl Chlorides

Cyclohexane with acetyl chloride and aluminum chloride yields 1-methyl-2-acetylcyclopentane, together with such by-products as condensed hydrocarbons. The reaction was reported by Nenitzescu and Ionescu,[38] who slowly added 300 g of acetyl chloride to a mixture of 600 g of aluminum chloride and 2000 cc of cyclohexane. After the reaction mixture had been stirred for three days it separated into two layers From the upper layer there was obtained the hydrocarbon, $C_{12}H_{22}$, b. 213-214°, and from the lower, 146 g of a yellow oil from which 1-methyl-2-acetylcyclopentane (b. 167-168°/759 mm) was secured through its semicarbazone. Obviously an isomerization of cyclohexane to methylcyclopentane occurred under the influence of the catalyst:

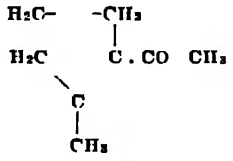
[36] U. S. P. 1,899,582 (1933), British P. 327,411 (1929), French P. 669,739 (1929), all to I. G. Farben industrie; *C. Z.*, 1930 I, 3237.
[37] U. S. P. 2,166,161 (1939) to H. Hopff, H. Kellermann, and A. Freytag (to I. G.); British P 477,778 (1936) to I. G., *Brit. Chem. Abs.*-B, 255 (1938).
[38] C. D. Nenitzescu and C. N. Ionescu, *Ann.*, 491, 189-210 (1931).



This subsequently reacted with acetyl chloride to give the ketone:



When acetyl chloride was added to a mixture of cyclohexane and aluminum chloride held at −18°, and the reaction mixture was kept at 20-22° for six days, and then at 28° for eight hours, Unger [39] reported that the unsaturated ketone,



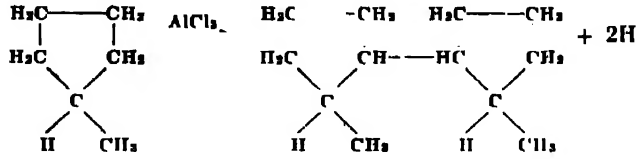
was also one of the reaction products. Evolution of hydrogen chloride was marked only at the higher temperatures.

Nenitzescu and Cantuniari [40] have shown that this compound is formed only if reaction is retarded. They found that, if commercial "anhydrous" aluminum chloride is used, the unsaturated product reported by Unger is secured; when freshly sublimed catalyst is employed, only the saturated ketone is formed. Catalyst poisons, for example, compounds with which aluminum chloride forms a molecular complex, similarly affect the course of the reaction. Since aluminum chloride forms complexes with nitrobenzene, or ketones like acetone, the course of the reaction in the presence of these substances results also in the formation of the unsaturated product.

In the presence of sufficient quantity of either acetone or methyl ethyl ketone, the reaction may be directed so as to give practically only the unsaturated ketone. It was also found by these workers [41] that unless an excess of the catalyst is used, the reaction yields a mixture of the saturated and unsaturated ketones.

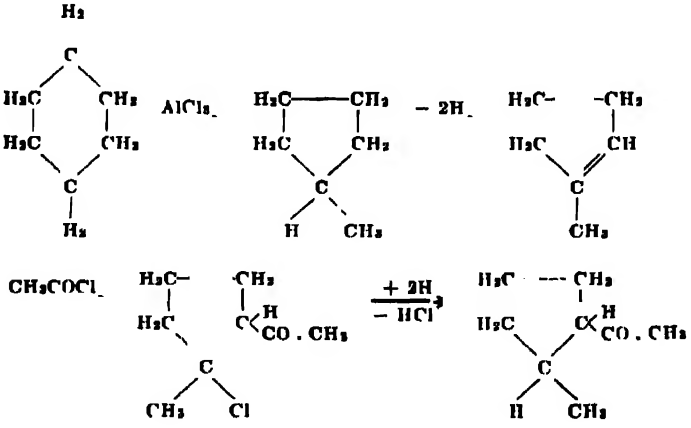
[39] F. Unger, *Ber.*, 65, 467-472 (1932).
[40] C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, 65, 1449-1453 (1932).
[41] C. D. Nenitzescu and I. P. Cantuniari, *Ann.*, 510, 269-279 (1934).

The influence of a weakened catalyst on the type of product obtained in the reaction between cyclohexane and acetyl chloride can be explained by an understanding of the mechanism of the reaction. In the preparation of the saturated ketone, the formation of condensed hydrocarbons occurs. Methylcyclopentane formed by the isomerizing action of aluminum chloride condenses with itself to form the hydrocarbon, $C_{12}H_{22}$, with liberation of two hydrogen atoms:

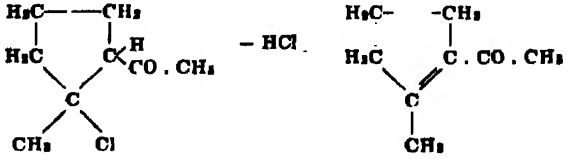


The labile hydrogen thus formed is needed for the formation of the saturated ketone. It is not available unless a sufficient quantity of aluminum chloride is present to allow formation of the hydrocarbon, $C_{12}H_{22}$, and more highly condensed hydrocarbons.

The formation of the saturated and/or the unsaturated ketone is believed by Nenitzescu and Cantuniari [41] to occur according to the mechanism:



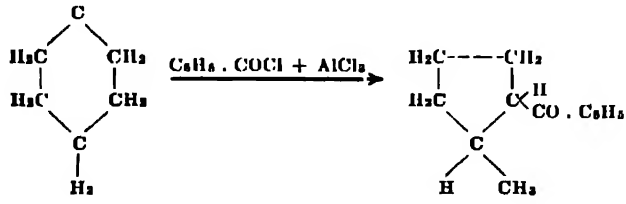
If the hydrogen is not available for the last reaction, however, there is only a dehydrohalogenation of the chloro-ketone,



and the unsaturated ketone is formed.

Previously, Hopff [42] had reported that the reaction of cyclohexane with acetyl chloride and aluminum chloride resulted in formation of acetylcyclohexane. Upon publication of the work of Nenitzescu, however, he repeated the preparation and found that in reality the product was 1-methyl-2-acetylcyclopentane.[43]

The presence of a small amount of water in the reaction of acetyl chloride or benzoyl chloride with cyclohexane has been observed to result in the formation of some acetaldehyde or benzaldehyde, although pure anhydrous aluminum chloride catalyzes the production of 1-methyl-2-benzoylcyclopentane:



The formation of the aldehydes has been explained by the fact that when a small amount of water is added to the aluminum chloride the hydrogen chloride liberated, effecting a higher solubility of the catalyst in the saturated hydrocarbon, causes increased catalytic activity. Consequently, enough hydrogen is evolved through self-condensation of cyclohexane:

$$2C_6H_{12} \longrightarrow C_{12}H_{22} + 2H$$

to reduce the acid chloride [44]:

$$C_6H_5COCl + 2H \longrightarrow C_6H_5CHO + HCl$$

The product obtained in the reaction of cyclohexane with acyl chlorides in the presence of aluminum chloride therefore depends essentially on the condition of the catalyst. Pure anhydrous catalyst yields a saturated ketone; the use of an activated catalyst leads also to the production of aldehyde, whereas the presence of compounds with which the catalyst forms molecular complexes results in a weakened catalyst which effects the formation of unsaturated ketones.

The results of Nenitzescu and co-workers have been questioned by Zelinsky and Tarassowa.[45] On the basis of much research [46] dealing with attempted acetylation of cyclic hydrocarbons of the C_5, C_6, and C_7 series, these investigators concluded that there is no difference in the type of product obtained in the aluminum chloride-catalyzed acylation of ali-

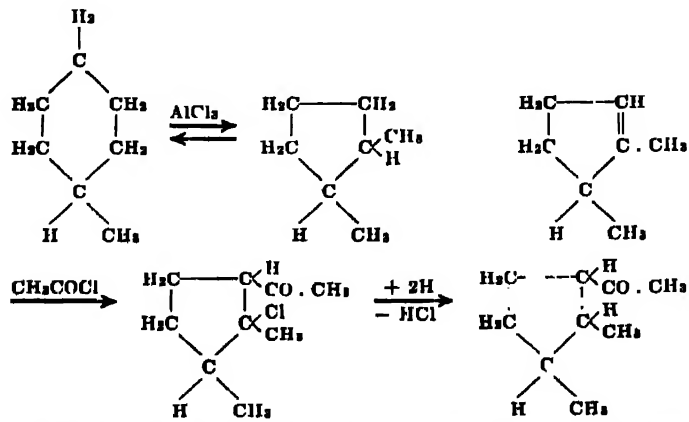
[42] H. Hopff, *Ber.*, **64**, 2739-2748 (1931); *C. A.*, **26**, 1230.
[43] H. Hopff, *Ber.*, **65**, 482-484 (1932).
[44] C. D. Nenitzescu and C. N. Ionescu, *Ann.*, **491**, 189-210 (1931). C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, **65**, 1449-1453 (1932).
[45] N. D. Zelinsky and E. M. Tarassowa, *Ber.*, **65**, 1249-1252 (1932); *Ann.*, **508**, 115-143 (1934).
[46] N. D. Zelinsky, *J. Russ. Phys-Chem. Soc.*, **30**, 341 (1898); **31**, 402 (1899); **34**, 866 (1902).

cyclic or of aromatic hydrocarbons. Alicyclic hydrocarbons were found by them to give very low yields of the corresponding acylated cycloalkanes. This conclusion was reached on the following bases:

1. The rearrangement of cyclohexane into methylcyclopentane in the Friedel-Crafts reaction is not always complete. It depends upon experimental conditions.
2. Reaction of cyclohexane with acetyl chloride under different conditions was found to give various yields of unsaturated ketone Thus with one mole each of cyclohexane and acetyl chloride and one or two moles of aluminum chloride, the product contains about 9 per cent of unsaturated ketone; with excess of cyclohexane it consists of 54 per cent unsaturated ketone. Using an acetylaluminum chloride complex the product contained 85 per cent unsaturated ketone.
3. Temperature plays a large part in governing the type of product obtained. If it is gradually allowed to reach 70°, the product is almost entirely saturated; if it is kept between 18-35°, the product is predominantly unsaturated.

Zelinsky and Tarassowa explained the production of saturated and unsaturated ketone by the fact that cyclohexane may react in two stereoisomeric forms. Acetylation of the *trans*-form gives a mixture of 1-methyl-2-acetylcyclopentane, acetylcyclohexane, and a little acetylcyclohexene The *cis*-form, on the other hand, is easily dehydrogenated during the reaction, so that the product is acetylcyclohexene.

Nenitzescu and his co-workers[47] repeated Zelinsky's work and obtained both unsaturated and saturated ketones These, however, they identified as 5-carbon ring ketones; they reported that in the reaction, 6-carbon ring ketones were not produced in any identifiable amounts The non-formation of 6-membered ring ketones was ascribed to the fact that the velocity of isomerization of cyclohexane to methylcyclopentane is greater than the speed of acetylation of cyclohexane. Various deriv-



[47] C. D. Nenitzescu and I. P. Cantuniari, *Ann.*, 510, 269-279 (1934). C. D. Nenitzescu and I. Chicos, *Ber.*, 68, 1884-1886 (1935).

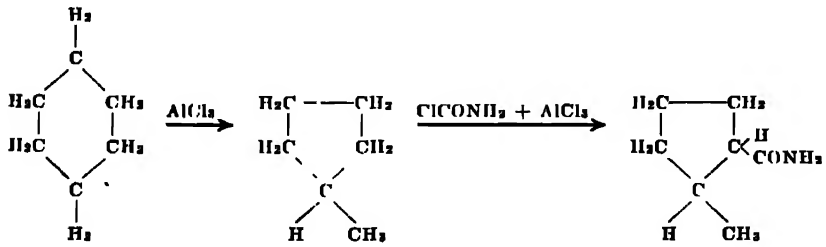
atives of 1-methyl-2-acetylcyclopentane, and the unsaturated ketone, 1-methyl-2-acetylcyclopentene, were prepared in order to establish the identity of these end-products.[48]

Methylcyclohexane also condenses with acetyl chloride and aluminum chloride with intermediate isomerization. The product of the reaction has been shown[49] to be 2,3-dimethyl-1-acetylcyclopentane, the condensation proceeding according to the scheme shown at bottom of page 750. The reaction proceeds as it does with cyclohexane.

With 5-membered rings, preliminary isomerization in Friedel-Crafts acylations is not apparent. From cyclopentane and acetyl chloride with aluminum chloride, there was obtained acetylcyclopentane, which was identified by conversion to cyclopentanecarboxylic acid and to its amide. Methylcyclopentane reacts very easily with acetyl chloride and yields 1-methyl-2-acetylcyclopentane, the same compound which is obtained by reaction of cyclohexane with acetyl chloride under similar conditions.[50]

The reaction of hydroaromatic hydrocarbons with acyl chlorides and aluminum chloride under pressure has been claimed, cyclohexane with benzoyl chloride being specifically cited.[51]

The condensation of cyclohexane with a molecular compound of carbamyl chloride and aluminum chloride during twelve hours at 130-140° in an autoclave has been claimed to result in production of 1-methylcyclopentane-2-carboxylic acid amide[52]:



The reaction of phenylcyclohexane with acetyl chloride has been reported by Mayes and Turner.[53] A 60 per cent yield of *p*-acetylphenylcyclohexane was reported.

Condensations involving other hydrogenated aromatic hydrocarbons are reviewed elsewhere.*

[48] C. D. Nenitzescu and G. G. Vantu, *Bull soc. de chimie din Romania*, 18, 1-2 (1936); *Bull. soc. chim. (5)*, 2, 2209 (1935).
[49] C. D. Nenitzescu, E. Cioranescu, and I. P. Cantuniari, *Ber.*, 70, 277-283 (1937).
[50] C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, 65, 807-812 (1932).
[51] U. S. P. 1,909,582 (1933), British P. 327,411 (1929), French P. 669,739 (1929), all to I. G. Farbenindustrie; *C. Z.*, 1930 I, 3237.
[52] U. S. P. 2,168,161 (1939) to H. Hopff, H. Kellermann, and A. Freytag (to I. G.); British P. 477,778 (1938) to I. G.; *British Chem. Abs.*-B, 255 (1938).
[53] H. A. Mayes and E. E. Turner, *J. Chem. Soc.*, 500-503 (1929).

* See page 294.

Reaction of Olefins with Acyl Halides

In 1908, Krapivin [51] reported the condensation of acyl halides with olefinic hydrocarbons in the presence of aluminum chloride or aluminum bromide. In order to avoid formation of addition or reaction products of only two components, low temperatures were used during simultaneous introduction of all three reactants into a solvent held at 0° or less Except with propylene or ethylene, carefully purified, dry carbon disulfide was used as solvent. With propylene or ethylene, commercial petroleum hexane was used. It had been previously freed of unsaturated and cyclic compounds by treatment with potassium permanganate, and after careful drying, with acetyl chloride and aluminum chloride with gentle heating. Varying yields of unsaturated ketones were obtained according to the general scheme:

$$RCH:CH_2 + CH_3COX \xrightarrow{AlX} R.CH:CH.CO\ CH_3 + HX$$

In all cases saturated chloroketones were also formed:

$$RCH:CH_2 + CH_3COX \xrightarrow{AlX} R.CHCl.CH_2.CO\ CH_3$$

Saturated chlorinated hydrocarbons of the general formula $C_nH_{2n+1}X$ were also isolated as by-products. If before the main reaction of all three components, only two components react with each other, there are formed only condensed unsaturated hydrocarbons.

Condensation of trimethylethylene with acetyl chloride was conducted by dissolving in carbon disulfide at 0° amounts of the reactants corresponding to the ratio $2C_5H_{10}:2CH_3COCl:AlCl_3$. Heating up to the boiling point of the solvent was slowly initiated, and the temperature was kept at that point for about two hours, at which time evolution of hydrogen chloride had ceased. Yield of unsaturated ketone was found to be increased if the reaction mixture was allowed to cool slowly before removal of solvent carbon disulfide and decomposition of the catalyst complex with ice-sodium carbonate. Steam distillation gave a fraction (b.p. 86°) which contained chlorine and was saturated, and another fraction (b.p. 143-144°) which was halogen-free and unsaturated. The pure unsaturated ketone, isolated through its semicarbazone, boiled at 144-145°/743 mm and was secured in a 20 per cent of theoretical yield. It was identified as 2,3-dimethyl-2-pentenone:

Under analogous conditions, hexene-2 gave a 30 per cent yield of the unsaturated ketone, $C_8H_{14}O$, and unsaturated ketones were similarly

[51] S. Krapivin, *Bull. soc. imp. Nat. Moscow*, 1-176 (1908); *C. A.*, **5**, 1981.

secured in 40 per cent yields from heptene-3 and from octene. In all cases the acyl radical replaced one of the hydrogen atoms of the olefin.

The condensation of ethylene with acetyl chloride did not progress so smoothly. Reaction was effected by dissolving 60 g of aluminum chloride in 500 cc of petroleum hexane, purified as noted above, and passing in 3 liters of ethylene while adding 28 g of acetyl chloride at −12° to −10° during six hours. The reaction mixture was allowed to stand for 15 hours in the cold before isolation of the products Only a very small amount of the expected vinyl methyl ketone was secured. The use of aluminum bromide instead of aluminum chloride, or of acetyl bromide instead of the corresponding halide, did not improve the yields materially.

In an analogous preparation, using 3 moles of propylene, 3 moles of acetyl bromide, and 4 moles of aluminum bromide in carbon disulfide solution an unsaturated ketone was secured whose constants were reported to be:

b p. 122-123°/740 mm.
$n_D^{25.5}$ 1 4323
$d_4^{25.5}$ 0 8659
molecular refraction 25.17

With hexane as solvent, and using the same reactants in a 3:3:2 ratio, the constants from the unsaturated ketone obtained were:

b p. 122-123°/741 mm.
n_D^{20}
d_4^{20} 0 8624
molecular refraction 25 41.

Both products were reported to be propenyl methyl ketone, $CH_3.CO.CH{:}CH.CH_3$, the varying constants indicating impurity of the preparations.

In this laboratory [55] the synthesis of *n*-propenyl methyl ketone was attempted by reacting molecular equivalents of propylene, acetyl chloride, and aluminum chloride. Reaction was effected in hexane solution at 0° for 2½ hours and then at 25° for 18 hours. A 71 per cent yield of a product having the following constants was secured:

b p. 89 5-91°/190 mm.
n_D^{20} 1 4346

The material was found to contain chlorine, and since the most likely chlorine-containing impurity was assumed to be the corresponding saturated chloroketone, the product was submitted to dehydrohalogenating agents. Using standard methods for this reaction, there resulted in every case a complex mixture of liquids having wide boiling ranges.

[55] R. Fordyce, Thomas and Hochwalt Laboratories Division, Monsanto Chemical Company.

Similar results have been secured with propylene and propionyl chloride in the presence of aluminum chloride in hexane solution at 0° for 1½ hours and for 48 hours at 25°. In this condensation a 72 per cent yield of a product (b.p. 109-109.2°/210 mm) was secured which was probably *n*-propenyl ethyl ketone, contaminated with traces of the corresponding saturated chloroketone.

Friedel-Crafts reaction of lauroyl chloride with propylene was also investigated in this laboratory.[56] An unsaturated chlorine-free ketone, probably undecyl propenyl ketone, $C_{11}H_{23}COCH{:}CHCH_3$, was prepared by adding 60 cc of liquid propylene to a solution of 100 g of lauroyl chloride in 400 cc of mixed hexanes kept at −40°, gradually raising the temperature to 0°, adding 61 g of aluminum chloride in small portions, and agitating the reaction mixture for five hours at about 0°. After decomposition of the product with ice-hydrochloric acid, washing with water, and then with potassium hydroxide and water, the solvent was evaporated and the residue was fractionated *in vacuo*. The following fractions were secured from a second fractionation:

Fraction	b.p.	Yield	n_d^{20}
1	82°/2 mm	1.5 g	1.4720
2	82-100°/2 mm	2.5 g	1.4720
3	117°/9 mm	2.0 g	1.4700
4	117-118°/9 mm	55.7 g	1.4580
5	residue	21.0 g	1.4789

Considerable hydrogen chloride was evolved during the fractionation. Fraction (4), secured in 54 per cent yield, was chlorine-free, whereas the residue was not.

That the production of unsaturated ketones from olefines in acyl halides proceeds through intermediate formation of saturated β-chloroketones may be assumed from data submitted by various investigators. In 1894 Kondakow[57] reported that the use of zinc chloride, a milder catalyst, in the reaction of trimethylethylene, isobutylene, or propylene with acetyl chloride results in formation of β-chloroketones. Wieland and Bettag[58] secured a 16.3 per cent yield of (α,β,β-trimethyl-β-chloroethyl) methyl ketone by adding 50 g of aluminum chloride during 1½ hours to a carbon disulfide solution of 10 g of trimethylethylene and 14 g of acetyl chloride at −18°. There was no noticeable evolution of hydrogen chloride, the reaction being one of simple addition:

$$(CH_3)_2C:CH(CH_3) + CH_3COCl \longrightarrow (CH_3)_2CCl.CH(CH_3).COCH_3$$

The chloroketone was found to be very unstable, decomposing with evolution of hydrogen chloride. According to these investigators, olefins evidently react with acid chlorides in the cold by adding acid chloride to the double bond; upon heating, the chlorinated ketones yield unsaturated ketones with cleavage of hydrogen chloride, thus:

[56] D. Aelony, Thomas and Hochwalt Laboratories Division, Monsanto Chemical Company.
[57] J. Kondakow, *J. Russ. Phys.-Chem. Soc.* **1894** I, 5-20; *Ber.*, **27**, Ref. 809 (1894).
[58] H. Wieland and L. Bettag, *Ber.*, **55**, 2246-2255 (1922).

$$RCH:CH_2 \xrightarrow{RCOCl} RCHCl.CH_2.COR \xrightarrow{-HCl} RCH:CH.COR$$

If acylation is not conducted at low temperature, the unsaturated ketone is the reaction product.

Anticipating that unsaturated compounds containing a double bond might replace unsaturated aryl hydrocarbons in the Friedel-Crafts reaction, Norris and Couch [59] investigated the condensation of ethylene with benzoyl chloride. A molecular complex of the acid chloride with aluminum chloride in carbon disulfide was first prepared, and ethylene was bubbled through a suspension of the crystallized complex in carbon disulfide. The gas was absorbed very slowly, and due to the fact that the crystals became covered with the oily reaction product, it was necessary to crush them during the reaction period in order to permit absorption of the gas by the complex. The oily product obtained in 25 per cent yield was shown to be phenyl vinyl ketone, the reaction having occurred in the expected fashion:

$$CH_2:CH_2 + C_6H_5COCl \longrightarrow C_6H_5COCH:CH_2 + HCl$$

Besides this, a small quantity of a product insoluble in carbon disulfide was formed. Its constitution was not established. No other side reactions seemed to occur.

More recently the production of β-chloropropiophenone by reaction of ethylene with benzoyl chloride and aluminum chloride has been studied by Allen, Cressman, and Bell.[60] The problem was found to be complicated by the fact that benzoyl chloride and aluminum chloride form a double compound, insoluble in most solvents, by the fact that ethylene must be introduced so as to become well admixed with the solution, and by the easy decomposition of the β-chloroketone. These difficulties were somewhat overcome by using ethyl bromide as solvent for the benzoyl chloride-aluminum chloride complex, by using a special "Pyrex" glass stirrer devised to introduce the ethylene into the solution under slight pressure, and by heating the final reaction mixture at temperatures not greater than 50° to drive off the solvent for isolation of the β-chloroketone. In this way yields of 87-92 per cent of β-chloropropiophenone were obtained.

The direct addition of chloroacetyl chloride to ethylene, using aluminum chloride as condensing agent, gives chloromethyl β-chloroethyl ketone. By passing ethylene for two hours into a petroleum ether solution of aluminum chloride while slowly adding 11.3 g of chloroacetyl chloride, a 2.8 g yield of the ketone is obtained.[61]

The manufacture of β-halogenoethyl alkyl ketones by reaction of ethylene with acyl halides and aluminum chloride has been patented.[62]

[59] J. F. Norris and H. B. Couch, *J. Am. Chem. Soc.*, 42, 2329-2332 (1920).
[60] C. F. H. Allen, H. W. J. Cressman, and A. C. Bell, *Can. J. Research*, 5, 440-446 (1933).
[61] R. H. Carroll and G. B. L. Smith, *J. Am. Chem. Soc.*, 55, 370-373 (1933).
[62] U. S. P. 1,737,309 (1929) to W. Schoeller and C. Zollner (to Schering-Kahlbaum; British P. 289,412 (1928) to Schering-Kahlbaum, *Brit. Chem. Abs.*-B, 51 (1930).

Methyl β-chloroethyl ketone (b.p. 50-55°/16 mm) and methyl β-bromoethyl ketone (b.p. 55-60°/15 mm) are claimed.

An interesting reaction is that claimed of ethylenic hydrocarbons with halogenated aliphatic carboxylic halides of not less than three carbon atoms.[63] Here the resulting chloroketones are dehydrohalogenated by heating with dimethylaniline to give ketones containing several unsaturated linkages. Thus ethylene with chloropropionyl chloride gives bis-(β-chloroethyl) ketone (b.p. 73-75°/12 mm), which is subsequently dehydrohalogenated to yield divinyl ketone:

$$CH_2 : CH_2 + CH_2Cl . CH_2 . CO . Cl \xrightarrow{AlCl_3} (CH_2Cl . CH_2)_2CO$$

$$\xrightarrow{\text{dimethylaniline}} (CH_2 : CH)_2 . CO$$

With propylene and chloropropionyl chloride and aluminum chloride there is obtained chloroethyl chloropropyl ketone (b.p. 85-90°/12 mm) which yields vinyl propenyl ketone, b.p. 40-45°/50 mm. Or, the condensation may be effected with an unsaturated aliphatic acid halide. Crotonyl chloride with propylene gives chloropropyl propenyl ketone, b.p. 50-55°/12 mm:

$$CH_3CH : CH_2 + CH_3CH : CHCOCl \xrightarrow{AlCl_3} CH_3 . CHCl . CH_2 . CO . CH : CH . CH_3$$

This, upon dehydrohalogenation, yields dipropenyl ketone, b.p. 50°/50 mm:

$$CH_3 . CHCl . CH_2 . CO\ CH:CHCH_3 \xrightarrow{\text{dimethylaniline}} CH_3 . CH.CH . CO . CH:CH . CH_3$$

Saturated β-chloroketones obtained by Friedel-Crafts acylation of olefins have been further reacted with benzene by Nenitzescu and Gavat.[64] When the complex obtained by reaction of ethylene with acetyl chloride and aluminum chloride was treated with benzene, 1-phenylbutanone-3 (b.p. 230-233°) was obtained in the normal reaction:

$$CH_2 : CH_2 + ClCOCH_3 \rightarrow ClCH_2CH_2COCH_3$$

$$\xrightarrow{C_6H_6} C_6H_5CH_2 . CH_2COCH_3 + HCl$$

These investigators led, with stirring, 1.5 moles of ethylene into a suspension of 133 g of aluminum chloride in 160 cc of carbon disulfide. After the aluminum chloride had liquefied, the carbon disulfide was decanted, and 200 cc of benzene was added. The reaction mixture was stirred for eight hours, and then worked up in usual fashion.

In a similar reaction with propene, 45 g of 2-phenylpentanone-(4), $CH_3CH(C_6H_5).CH_2.CO.CH_3$ (b.p. 113-115°/13 mm) was obtained from 40 liters of propylene, 87 g of acetyl chloride, and 300 cc of benzene

[63] British P. 459,537 (1935) to I. G. Farbenindustrie; *Brit. Chem. Abs.*-B, 215 (1937)
[64] C. D. Nenitzescu and I. G. Gavat, *Ann.*, 519, 260-271 (1935).

A like reaction occurred with butene-2; when butene-1 was used, however, halogen migration occurred. The reaction should have proceeded:

$$CH_3.CH_2.CH:CH_2 + ClCOCH_3 \rightarrow CH_3.CH_2.CHCl.CH_2.CO.CH_3$$

$$\overset{C_6H_5}{CH_3.CH_2.CH}.CH_2CO.CH_3 + HCl$$

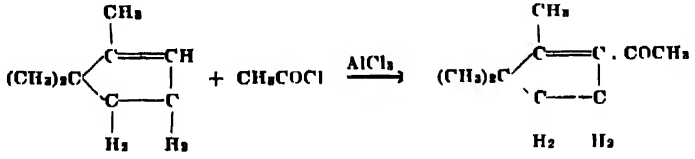
Instead, the product was 5-phenylhexanone-2,

$$CH_3.\overset{C_6H_5}{CH}.CH_2.CH_2.CO.CH_3$$

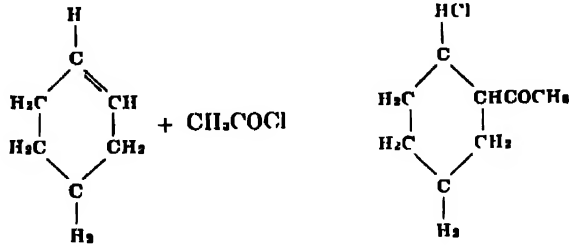
Obviously the aluminum chloride effects migration of the halogen to a remote carbon atom, but not so far as to the terminal methyl group.

Reaction of Alicyclic Olefins with Acyl Halides

In an early study dealing with the constitution of isolauronolic acid, it was noticed by Blanc[65] that when 1,1,2-trimethyl-2-cyclopentene was dissolved in carbon disulfide and treated with acetyl chloride in the presence of aluminum chloride, the corresponding unsaturated ketone was produced:



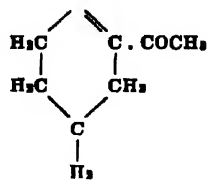
Working at a temperature of 0°, Darzens[66] added aluminum chloride to a mixture of acetyl chloride and cyclohexene in carbon disulfide, and secured first a saturated chloroketone:



Upon treatment with dimethylaniline, this ketone easily split off hydrogen chloride to give 1-acetylcyclohexene,

[65] G. Blanc, *Bull. soc. chim (3)*, 19, 699-706 (1898); *J. Chem Soc. Abs.*, 76 (I), 680 (1899).
[66] G. Darzens, *Compt. rend.*, 150, 707-710 (1910); *C. Z.*, 1910 I, 1785.

II



The unsaturated ketone was obtained in a 42 per cent of theoretical yield, based on the initial reactants. It was pointed out by Darzens that this seemed to be a very general reaction for hydrocarbons containing an olefinic linkage.[67]

Wieland and Bettag[68] reported that the formation of the chloroketone depended on the use of low temperatures, and that quantitative conversion to the unsaturated ketone could be effected by subsequent heating of the chloroketone in the presence of a trace of aluminum chloride. These investigators added, with stirring, during two hours 35 g of aluminum chloride to a solution of 20 g of cyclohexene and 30 g of acetyl chloride in 75 g of carbon disulfide. The temperature was maintained at −18°. The resulting complex contained about 70 per cent of the chloroketone, and some unsaturated ketone, 1-acetylcyclohexene, which could not be separated by distillation. The isolated chloroketone (b.p. 60-63°/1 mm) was converted into the unsaturated ketone by dissolving it in carbon disulfide and adding 0.5 g of aluminum chloride to the solution, with strong cooling. As the temperature was allowed to increase, evolution of hydrogen chloride began. After ten hours no hydrogen chloride cleavage was noticeable, even upon boiling. This procedure gave a 60 per cent of theoretical yield of unsaturated ketone, based on the original reactants.

Similar treatment of cyclohexene with benzoyl chloride resulted in much lower yield. Only a 13 per cent yield of the chloroketone was obtained, and its conversion into the unsaturated ketone was only 45 14 per cent of theoretical. However, even lower yields of unsaturated ketone were secured when the reaction was performed without intermediate isolation of the chloroketone. In this case a considerable quantity of a polymerization product was secured. Obviously most of the 1-benzoylcyclohexene was polymerized by the aluminum chloride during the course of the reaction.

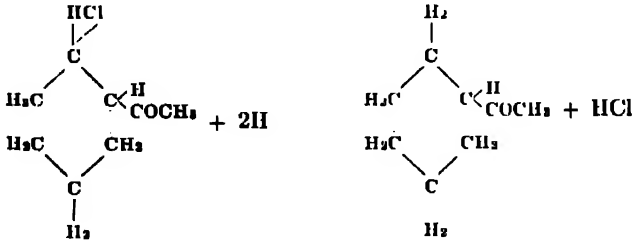
1-Benzoylcyclopentene has been secured in 32 per cent yield by treating 20 g of cyclopentene and 43 g of benzoyl chloride in 180 g of carbon disulfide with 44 g of aluminum chloride at −5° and then heating the crude addition product with 28 g of diethylaniline at 180° for three hours.[69]

[67] G. Darzens and H. Rost, *Compt. rend.*, 151, 758-759 (1910).
[68] H. Wieland and L. Bettag, *Ber.*, 55, 2246-2255 (1922); *cf.* R. E. Christ and R. C. Fuson, *J. Am. Chem. Soc.*, 59, 893-898 (1937).
[69] R. C. Fuson, R. Johnson, and W. Cole, *J. Am. Chem. Soc.*, 60, 1894-1898 (1938); *C. A.*, 32, 6230

In this laboratory[70] the preparation of 1-caproylcyclohexene by Friedel-Crafts reaction of cyclohexene with caproyl chloride and subsequent dehydrohalogenation of the product has been effected. During twenty minutes, 99 g of aluminum chloride was added to a solution of 100 g of the acid chloride and 100 g of cyclohexene in 200 cc of mixed hexanes. The mixture was agitated for five hours at 0°, and was allowed to stand over night. Upon decomposition of the reaction product with ice-hydrochloric acid, washing repeatedly with water, sodium hydroxide, and again water the product was dried over calcium chloride and filtered. After evaporation of the solvent, the product was distilled *in vacuo;* and the distillate, weighing 137 g, was dehydrohalogenated by heating with 80 g of nickel carbonate at 140° for 17 hours. The nickel carbonate was then filtered off, and the filtrate was fractionated twice *in vacuo*. The fraction (b.p. 90-95°/1.4 mm) obtained in 50 per cent yield, was chlorine-free and unsaturated. Its molecular weight, calculated from the Lorenz-Lorentz equation, was 179.2; that of 1-caproylcyclohexene is 180. Other constants of the product were as follows:

$$n_D^{20}\ 1.4803$$
$$d_4^{20}\ 0.9255$$

According to Nenitzescu and Cantuniari,[71] if the complex resulting from the low-temperature acetylation of cyclohexene is treated with cyclohexane in the presence of an excess of aluminum chloride, a very good yield of acetylcyclohexane results. This is ascribed to the dehydrohalogenating action of the nascent hydrogen formed by the aluminum chloride-catalyzed self-condensation of cyclohexane:



The hydrogen was obtained in the reaction:

$$2C_6H_{12} \qquad C_{12}H_{22} + 2H$$

This procedure was also illustrated in the acylation of cyclohexene in the presence of cyclohexane.[72] Here a mixture of one mole each of cyclohexene and acetyl chloride in cyclohexane was cooled to −15° and treated under stirring with 2 moles of aluminum chloride in small portions. Evolution of hydrogen chloride did not begin until the temperature had been

[70] D. Aelony, Thomas and Hochwalt Laboratories Division Monsanto Chemical Company.
[71] C. D. Nenitzescu and I. P. Cantuniari, *Ann.*, 510, 269-279 (1934).
[72] C. D. Nenitzescu and E. Cioranescu, *Ber.*, 69, 1820-1823 (1936).

increased. The reaction mixture was finally heated on a water-bath at 70° until evolution of hydrogen chloride had ceased. In this way 67 g of acetylcyclohexane was secured.

Similar reaction of cyclopentene with acetyl chloride gave acetylcyclopentane in a 50 per cent of theoretical yield. Use of this procedure in the reaction of cyclopentene with cyclopentanecarboxylic acid chloride and also with cyclohexanecarboxylic acid chloride for the production of dicyclic saturated ketones shows the general applicability of the reaction. Under the same conditions cyclohexene was reacted with 1-methylcyclopentane-2-carboxylic acid chloride and with isovaleryl chloride to give (2-methylcyclopentyl) cyclohexyl ketone and isobutyl cyclohexyl ketone, respectively. These syntheses show that under the conditions used in Friedel-Crafts acylations dehydrogenation of cyclohexane does result. When condensation is effected in the presence of carbon disulfide instead of cyclohexane, chloro-ketones result: cyclohexene and isovaleroyl chloride or caproyl chloride yield 1-chloro-2-isovaleroylcyclohexane and 1-chloro-2-caproylcyclohexane, respectively

Condensation of cyclohexene with benzoyl chloride in the presence of cyclohexane and aluminum chloride yields benzoylcyclohexane.[73]

The fact that acid chlorides add to olefinic double bonds in the presence of aluminum chloride has suggested the possibility of applying the reaction to the synthesis of unsaturated ketones of the chloresterol series. Accordingly, Wieland and Hasegawa [74] reacted cholesterol with acetyl chloride and aluminum chloride. The product (m.p. 151°) had the composition of an acetyl chloride addition product of chloresterol, but it was an ester, not a ketone.

Esters have also been reported to be the products of the reaction of hexachlorocyclohexadiene-1,4-one-3 and acyl halides in carbon disulfide solution in the presence of aluminum chloride.[75] Pentachlorophenyl acetate, propionate, or butyrate is thus secured from acetyl, propionyl, or butyryl chlorides respectively.

Reaction of Acetylene with Acid Chlorides

The Friedel-Crafts ketone synthesis has been extended to the acylation of acetylenic hydrocarbons. In the presence of aluminum chloride, acetylene has been reacted with acetyl chloride at 15° to form methyl β-chlorovinyl ketone (b.p. 135°) in a 25 per cent yield.[76]

According to recent patents,[77] much better yields may be secured. The process is claimed to be applicable to acetylene or its homologs, for example, methyl, ethyl, or phenyl acetylene or heptine. Carboxylic acid halides which are suitable for the reaction are acetyl, propionyl, butyryl, isovaleroyl, stearoyl, or benzoyl chlorides. The reaction proceeds:

$$RC{:}CH + R'COCl \qquad R'.CO.CH{:}CRCl$$

[73] C. D. Nenitzescu and J. Gavat, *Ber.*, **70**, 1685–1686 (1937).
[74] H. Wieland and Chohachi Hasegawa, *Ber.*, **64**, 2510–2522 (1931); *C. A.*, **26**, 477.
[75] E. Barral, *Bull. soc. chim. (3)*, **13**, 540–545 (1895).
[76] A. Cornillot and R. Alquier, *Compt. rend.*, **201**, 537–538 (1935).
[77] U. S. P. 2,125,333 (1938), Brit. P. 461,060 (1937), German P. 643,147 (1937) all to Johannes Nelles and Otto Bayer, (to I. G. Farbenindustrie); *C. A.*, **31**, 8401.

In the preparation of a β-halogenated vinyl ketone from isovaleroyl chloride and acetylene, 8 parts of aluminum chloride are added while stirring, and while introducing acetylene at a temperature of 0-5° to a solution of 10 parts of isovaleroyl chloride in 20 parts of petroleum ether. After some hours the reaction mixture is decomposed with ice water and extracted with benzene. Upon washing with a solution of potassium carbonate and evaporation of the benzene, isobutyl β-chlorovinyl ketone is secured in 85 per cent yield.

Heptadecyl chlorovinyl ketone has been obtained by passing acetylene into a solution of stearoyl chloride in carbon tetrachloride solution in the presence of aluminum chloride.[78]

Reaction of Acid Chlorides with other Aliphatic Compounds

Vinyl Halides.—Halogenated unsaturated ketones may be secured by reaction of vinyl halides with acid halides in the presence of aluminum chloride at ordinary temperature and pressure.[79] Vinyl chloride and benzoyl chloride thus yield phenyl chlorovinyl ketone, b_{18} 133-135°:

$$ClCH : CH_2 + C_6H_5COCl \xrightarrow{AlCl_3} ClCH : CH . CO . C_6H_5$$

Analogously, acetyl chloride yields chlorovinyl methyl ketone, (b_{18} 43-45°) and isovaleroyl chloride yields the expected isobutyl β-chlorovinyl ketone, b_{18} 72-74°.

Reaction may be effected in carbon tetrachloride as solvent. That condensation probably proceeds through intermediate formation of a saturated product is evident from the fact that during distillation of the crude product under reduced pressure, hydrogen chloride is eliminated.[80]

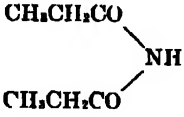
Aliphatic Nitriles.—Aromatic nitriles react with aliphatic acid chlorides in the presence of aluminum chloride to give substituted triazines.[81] With aromatic acid chlorides under like conditions, dibenzamides are formed.[82] Diamides are likewise formed in the reaction of aliphatic acid chlorides with aliphatic nitriles.

In a preliminary communication, Otto and Tröger[83] reported that when aluminum chloride is added to a mixture of propionitrile and propionyl chloride, and the reaction mixture heated for a short time on a water-bath to complete the condensation, 2-amidopentanone-3 was secured through primary formation of the keto-nitrile:

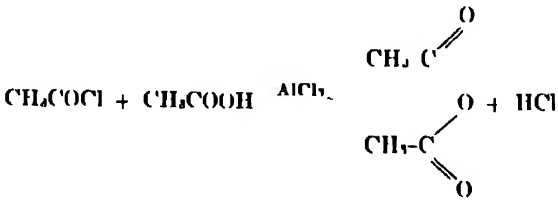
$$CH_3 . CH_2CN \xrightarrow{C_2H_5COCl + AlCl_3} CH_3 . \underset{\displaystyle CN}{\underset{|}{CH}} . CO . C_2H_5 \xrightarrow{H_2O} CH_3 . \underset{\displaystyle CONH_2}{\underset{|}{CH}} . CO . C_2H_5$$

[78] Brit. P. 466,402 (1936) to I. G. Farbenindustrie; *C. A.*, 33, 4356
[79] U. S. P. 2,167,694 (1939) to O. Bayer and J. Nelles (to I. G.); *C. A.*, 33, 1758.
[80] Brit. P. 466,801 (1937) to I. G. Farbenindustrie; *Brit. Chem. Abs.*-B, 759 (1937).
[81] F. Krafft and A. v. Hansen, *Ber.*, 22, 808-811 (1889).
[82] F. Krafft, *Ber.*, 23, 2890-2893 (1890).
[83] R. Otto and J. Tröger, *Ber.*, 22, 1455-1456 (1889); *J. Chem. Soc. Abs.*, 56, 987 (1889).

Further investigation showed,[84] however, that the product was probably dipropionamide, m.p. 153-154°.



Carboxylic Acids.—A rather unusual application of aluminum chloride in aliphatic chemistry is the production of acid anhydrides by reaction of an acid chloride with the corresponding acid:



Thus, to produce an anhydride such as butyric anhydride, butyric acid and the corresponding acid chloride are caused to react at about 182° in the presence of a small amount of aluminum chloride serving as a catalyst.[85]

The reaction may be similarly applied to the production of halogenated acid anhydrides. Chloroacetic anhydride is obtained by heating chloroacetyl chloride with chloroacetic acid in the presence of about 1 per cent of aluminum chloride.[86]

Alcohols.—An interesting reaction, described in 1887, but apparently little used, is that of acid chloride-aluminum chloride complexes with alcohols.[87] When an aliphatic acid chloride is treated with aluminum chloride in carbon disulfide or chloroform, a solid crystalline compound is formed, with evolution of hydrogen chloride. The complex, $(CH_3CO)_2$-$CH.CCl_2.O.AlCl_2$, is obtained by gradual addition of 91 g of aluminum chloride to 158 g of acetyl chloride dissolved in 522 g of chloroform at 50°. The complex is violently decomposed upon addition of water, with formation of acetylacetone. When it is added in small portions to well-cooled ethyl alcohol, an energetic reaction takes place with evolution of hydrogen chloride. Upon pouring this reaction mixture into water, there separates a reddish liquid which is a mixture of ethyl acetate, ethyl acetoacetate, and ethyl diacetoacetate, $(CH_3CO)_2CH.COOC_2H_5$. The main product of the reaction is ethyl diacetoacetate; the readiness with which

[84] R. Otto and J. Trüger, *Ber.*, 23, 759-768 (1890).
[85] U. S. P. 2,060,195 (1937) to Stefan Goldschmidt and R. R. Wolff (to Kessler Chemical Corporation); *C. A.*, 31, 420 (1937).
[86] U. S. P. 1,718,104 (1929) to C. J. Strosacker and C. C. Schwegler (to Dow Chemical Co.); *Brit. Chem. Abs.-B*, 557 (1929).
[87] A. Combes, *Compt. rend.*, 103, 814-817 (1886), *J. Chem. Soc. Abs.*, 52, 127 (1887); *Compt. rend.* 104, 855-858 (1887), *J. Chem. Soc. Abs.*, 52, 556 (1887); *Ann. chim. (6)*, 12, 205-255 (1887); G. Gustavson, *J. prakt. Chem. (2)*, 37, 109 (1888).

it splits up in the presence of alcohol is responsible for the formation of ethyl acetoacetate and ethyl acetate in this reaction.

Ethers.—Under certain conditions, aluminum chloride catalyzes the formation of esters from diethyl ether and an acid chloride.[88] Shah[89] has pointed out that dry ether can be used as solvent in Friedel-Crafts reactions only when the reactions take place below the boiling point of ether; otherwise the ether may enter into the condensation. The reaction of the complex $(C_2H_5)_2O.AlCl_3$ with acetyl chloride, acetic anhydride, benzoyl chloride, or benzoic anhydride was studied.[90] The most probable mechanism of the reaction of the ether complex with acetic anhydride was believed to be:

$$(C_2H_5)_2O \cdot AlCl_3 + (CH_3CO)_2O \longrightarrow 2CH_3COOC_2H_5 + AlCl_3$$

With acetyl chloride the scheme was believed to be:

$$(C_2H_5)_2O \cdot AlCl_3 + CH_3COCl \longrightarrow CH_3COOC_2H_5 + C_2H_5Cl + AlCl_3$$

The liberation of ethyl chloride in the process of the reaction was demonstrated.

A 70 per cent yield of ethyl acetate was secured by gradually adding, with cooling, 30 g of acetyl chloride to 45 g of anhydrous aluminum chloride in 100 cc of dry ether, and refluxing the mixture in a water-bath for six to eight hours. An 80 per cent yield of ethyl benzoate was similarly obtained with benzoyl chloride. With acid anhydrides, much lower yields of ester were obtained; acetic anhydride gave 14 per cent of ethyl acetate, and benzoic anhydride, 20 per cent of ethyl benzoate.

Reactions with Phosgene

Olefins.—Since phosgene may be considered as an acid halide, that is, as the chloride of chloroformic acid, or the dichloride of carbonic acid, it may be expected that its reaction with olefins would resemble that of acid halides. With ethylene, for example, the formation of β-chloropropionyl chloride would be expected:

$$CH_2 : CH_2 + COCl_2 \xrightarrow{AlCl_3} CH_2ClCH_2COCl$$

According to Pace,[91] who summarized the contradictory results which have been obtained in reacting phosgene with olefins, the course of the reaction is dependent on the presence or absence of aluminum chloride during the reaction. Using toluene as a solvent, he reported that phosgene and ethylene in the presence of aluminum chloride form β-chloropropionyl chloride which can be recovered from the toluene layer after neutralization. Subsequent investigations of this reaction have not con-

[88] H. P. Kaufmann and C. Fuchs, *Arch. Pharm.*, 262, 119-125 (1924). *J. Chem. Soc. Abs.*, 126 (I), 901 (1924). E. Wedekind and J. Haeussermann, *Ber.*, 34, 2081-2082 (1901).
[89] R. C. Shah, *Current Science*, 3, 157 (1934); *C. A.*, 29, 1072.
[90] N. S. Kozlov, R. Bogdanovskaya, and I. Sologub, *J. Gen. Chem. (U. S. S. R.)*, 6, 315-317 (1936); *C. A.*, 30, 4813.
[91] E. Pace, *Gazz. chim. ital.*, 59, 578-590 (1929); *C. A.*, 24, 338.

firmed these results,[92] the products formed being mainly ditolyl ketone and ethyltoluenes. Carbon tetrachloride was equally ineffective as a solvent, but by conducting the reaction in carbon disulfide and esterifying below 0°C with methyl alcohol it was found possible to prepare a 20-30 per cent yield of methyl β-chloropropionate by vacuum distillation. Atmospheric distillation of the product split off hydrogen chloride to form methyl acrylate.

An extension of the latter type of reaction to propylene [93] is the basis of a rather new method for the preparation of esters of methacrylic acid Phosgene and propylene in a molar ratio of 1 to 1 are passed into an autoclave containing β-chloroisobutyryl chloride in which 2-15 per cent of aluminum chloride is dissolved. The reaction is conducted at 30-100° and under 10-40 atmospheres' pressure. The product is drained off periodically, and more catalyst added to the residue to maintain the catalytic activity. The condensation proceeds:

$$COCl_2 + CH_2:CHCH_3 \longrightarrow CH_2Cl.\overset{CH_3}{\underset{|}{C}}H.COCl$$

The β-chloroisobutyryl chloride thus obtained is esterified and subsequently dehydrohalogenated to form esters of methacrylic acid:

$$CH_2Cl.\overset{CH_3}{\underset{|}{C}}H.COCl \xrightarrow{ROH} CH_2Cl\overset{CH_3}{\underset{|}{C}}H.COOR \xrightarrow{-HCl} CH_2:\overset{CH_3}{\underset{|}{C}}.COOR$$

Pace [91] reports that by bubbling phosgene for two to twenty hours at 35-40° into a mixture of isoamylene and aluminum chloride in toluene solution, β-chloroisocaproyl chloride is formed:

$$COCl_2 + (CH_3)_2CH.CH:CH_2 \longrightarrow (CH_3)_2CHCHClCH_2COCl$$

Unsaturated Alcohols.—Under the same conditions as those observed in the reaction of phosgene and isoamylene noted above Pace observed that when unsaturated alcohols were used instead of olefins, the products were chlorolactones. He assumes the intermediate formation of unstable addition compounds which are converted into lactones by elimination of hydrogen chloride. Allyl alcohol gives β-chloro-γ-butyrolactone, probably according to the scheme:

$$CH_2:CH.CH_2OH + COCl_2 \longrightarrow ClOC.CH_2.CHCl.CH_2OH$$

$$\xrightarrow{-HCl} CH_2.CHCl.CH_2.C:O$$

$$\underset{|\text{-----}-O|}{}$$

[92] P. K. Frolich and P. J. Wiezevich, *Ind. Eng. Chem.*, 24, 13-17 (1932). S. I. Vasilyevskii and Buruganyevskaya, *Gazz. chim. ital.*, 64, 53-59 (1934); *C. A.*, 28, 5043. A. L. Klebanskii and K. K. Chevruchalova, *Compt. rend. acad. sci. U. R. S. S.*, 2, 42-44 (1935); *C. A.*, 29, 5814; *J. Gen. Chem. (U. S. S. R.)*, 5, 535-548 (1935); *C. A.*, 29, 6879; *Trans. sci. Inst. Peoples' Commissar. Heavy Ind. U. S. S. R. State Inst. appl. chem. No.* 31, 46-62 (1937); *C. Z.*, 1938 I, 1335.

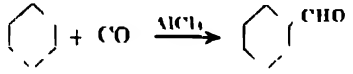
[93] U. S. P. 2,028,012 (1936) to E. E. Reid (to du Pont).

Paraffins.—Saturated paraffins and cycloparaffins are converted to ketones by treatment with phosgene and aluminum chloride at about 0°.[94] Reaction may be effected with cyclohexane, isopentane, or *n*-hexane.

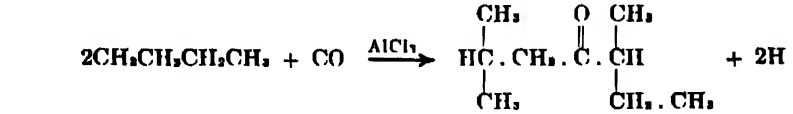
A double compound of phosgene and aluminum chloride, obtained by incorporating 5 parts of liquid phosgene with 2 parts of aluminum chloride may be reacted with paraffins under pressure to give a mixture of ketones.[95] The paraffin constituent may be a low-boiling petroleum fraction. A quantitative conversion into ketones of the polymethylene and paraffin series is said to take place.

Reactions with Carbon Monoxide

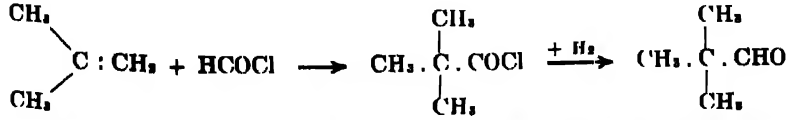
Paraffins.—The reaction of carbon monoxide with aromatic hydrocarbons and aluminum chloride is the well-known Gattermann method of aldehyde synthesis:



With paraffinic hydrocarbons, however, the reaction proceeds in entirely different fashion, yielding ketones. With butane, for example, the main reaction product is isobutyl *sec*-butyl ketone:

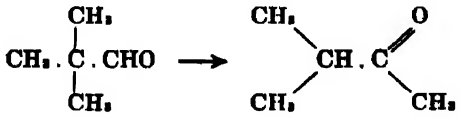


As reported by Hopff,[96] however, the reaction is not as simple as the above equation would lead one to expect. A number of side reactions occur, leading to the formation of methylacetic acid, trimethylacetic acid, and methyl isopropyl ketone as by-products. The hydrocarbon chain appears to have been cracked and isomerized during the reaction, and the carbon monoxide introduced between the cleavage fragments. A reaction scheme, assuming the intermediate formation of an aldehyde and subsequent isomerization of aldehyde to ketone, has been advanced.[97] With isobutane there is first dehydrogenation, leading to the formation of isobutene. Formyl chloride, HCOCl, is probably formed from the evolved hydrogen, carbon monoxide, and aluminum chloride. This reacts with the isobutene to form trimethylacetyl chloride, which is subsequently reduced to trimethylacetaldehyde:

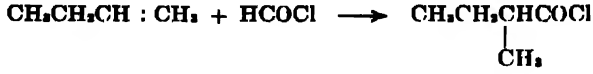


[94] U. S. P. 1,995,782 (1935) to A. Schnarschmidt, *C. A.*, **29**, 3349; Swiss P 165,822 (1934) to Antarox Trust Registered, *C. A.*, **28**, 2724.
[95] British P. 327,411 (1928) to I. G. Farbenindustrie; *Brit. Chem. Abs.*-B, 602 (1930).
[96] H. Hopff, *Ber.*, **64**, 2739-2748 (1931); **65**, 483-484 (1932); *Angew. Chem.*, **49**, 553 (1936).
[97] H. Hopff, C. D. Nenitzescu, D. A. Isacescu, and I. P. Cantuniari, *Ber.*, **69**, 2244-2251 (1936).

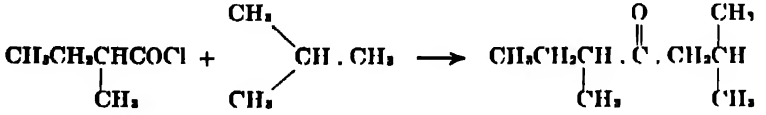
The trimethylacetaldehyde is then isomerized to methyl isopropyl ketone:



In the reaction with *n*-butane isomerization and dehydrogenation both occur. The *n*-butene formed reacts with formyl chloride as in the foregoing scheme to give the acid chloride:

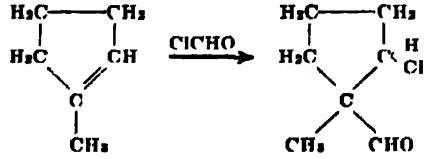


This then may react with the isobutane present to give isobutyl *sec*-butyl ketone:

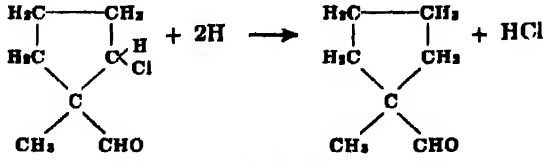


Along with this, of course, is also formed methyl isopropyl ketone, as shown in the scheme for isobutane, since a part of the *n*-butane isomerizes to isobutane and reacts as such.

The condensation of cyclohexane with carbon monoxide has also been studied. Hopff [98] reported the production of 1-methyl-2-cyclohexanone from the reaction. It was shown [99] that the action of carbon monoxide on cyclohexane consists of an initial isomerization of the cyclohexane into methylcyclopentane and subsequent dehydrogenation to methylcyclopentene. This is then converted by the formyl chloride into a chloroaldehyde,

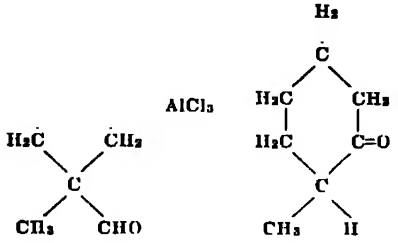


which is reduced by hydrogen evolved during the reaction to 1-methyl-1-formylcyclopentane:



[98] H. Hopff, *Ber.*, **65**, 483-484 (1932); *C. A.*, **26**, 2069.
[99] C. D. Nenitzescu and D. V. Ourcanoanu, *Ber.*, **71**, 2063-2065 (1938); *C. A.*, **33**, 145; *Brit. Chem. Abs.*-B, 494 (1938).

This is then isomerized to 2-methylcyclohexanone, the final reaction product:



The course of the reaction has been verified by the fact that 1-methyl-1-formylcyclopentane has been synthesized and converted almost quantitatively into 2-methylcyclohexanone.

Although condensation of carbon monoxide with paraffins does not result in the production of high yields of any one ketone, the process has been covered by several patents.[100] These patents generally specify the use of elevated pressures to maintain liquid phase. In the reaction of pentane with carbon monoxide, for example,[101] a high-pressure retort is charged with 100 parts of *n*-pentane and 100 parts of aluminum chloride. Carbon monoxide is admitted under a pressure of 120-150 atmospheres, and the retort is heated to a temperature of 35-60°. Absorption of carbon monoxide is noted by drop in pressure; carbon monoxide is forced into the reaction vessel until the original pressure has been reached, and no further drop in pressure occurs. The reaction products consist of a fraction (b.p. 114-116°), which is ethyl isopropyl ketone, and the main fraction (b.p. 116-250°), comprising a mixture of higher ketones which have probably been produced by condensation of ethyl isopropyl ketone under the influence of aluminum chloride. High-boiling carboxylic acids were also formed in the reaction.

The condensation may be similarly effected with other aliphatic or hydroaromatic hydrocarbons, or mixtures of such hydrocarbons, as well as with products of the destructive hydrogenation of such substances as coal, tar, mineral oils, lignite, tar-oils, and the like.

Alkyl Halides.—Halogenated paraffins also form acids and ketones when treated with carbon monoxide and aluminum chloride and the reaction product hydrolyzed. Thus, treatment of ethyl chloride or *n*-butyl chloride with aluminum chloride and subsequent reaction with carbon monoxide under pressure yields a product consisting of higher carboxylic acids and ketones. With ethyl chloride, for example, about 50 per cent of the reaction product is propionic acid. The action of carbon monoxide on *n*-butyl chloride and aluminum chloride at 50° and 120

[100] French P. 735,786 (1931), British P. 388,734 to A. Schaarschmidt; German P. 568,129 (1928), German P. 512,718 (1927), French P. 671,241 (1928), British P. 310,488 (1928), U. S. P. 1,801,080, and U. S. P. 1,801,350 (1931) all to I. G. Farbenindustrie; *C. Z.*, 1930 II, 620; German P. 520,164 (1927) to H. Hopff.

[101] British P. 310,488 (1928) to I. G. Farbenindustrie; *C. Z.*, 1929 II, 214.

atmospheres results in a product consisting mainly of an acid, $C_5H_{10}O_2$, together with higher homologs and ketones.[102]

Dialkyl Ethers.—Aluminum chloride has been mentioned as an optional catalyst in the preparation of aliphatic esters by reaction of carbon monoxide with dialkyl ethers.[103] The process, conducted at elevated temperatures and high pressure, consists in the preliminary formation of an ether-aluminum chloride complex and subsequent treatment of the complex with carbon monoxide. With ethyl ether, for example, the reaction may be assumed to proceed:

$$(C_2H_5)_2O \cdot AlCl_3 + CO \qquad C_2H_5COOC_2H_5 \cdot AlCl_3$$

The ethyl propionate is readily removed from the ester-aluminum chloride complex by treatment of the complex with ether, which preferentially enters into the complex, thus freeing the ester.

Reaction of Olefins with Acids

Aluminum chloride is one of the catalysts which effects condensation of olefins with aliphatic monocarboxylic acids for the preparation of esters:

$$CH_2CH : CH_2 + CH_3COOH \qquad \begin{matrix} CH_3 \\ \diagdown \\ CH \cdot COOCH_3 \\ \diagup \\ CH_3 \end{matrix}$$

Although the use of this catalyst has been claimed in several patents,[104] the reaction is more commonly effected with sulfuric acid, or one of the less active metal halides. A detailed treatment of the condensation is not, therefore, properly within the scope of this discussion.

Reaction of Olefins with Alcohols

The direct addition of olefins to alcohols, with production of ethers, is catalyzed by aluminum chloride, although as in the esterification of olefins, sulfuric acid is the best of the catalysts which have been investigated for this reaction.[105] With methanol, the general reaction is:

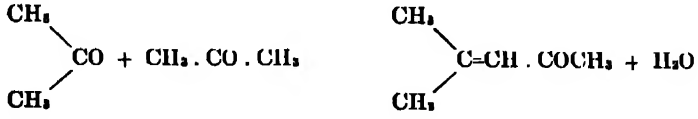
$$CH_3OH + C_nH_{2n} \qquad CH_3OC_nH_{2n+1}$$

The primary alcohols have been found to be more suitable for this reaction than the secondary alcohols; the tertiary alcohols are least reactive. Those olefins which can be derived theoretically from a tertiary alcohol, for example, trimethylethylene or isobutylene, are most suitable.

[102] German P. 568,129, U. S. P. 1,891,930 (1932) French P. 671,241 (1928) all to I. G. Farbenindustrie; *C. Z.*, 1930 II, 820; British P. 310,438 (1928) to I. G. Farbenindustrie; *C. Z.*, 1929 II, 214.
[103] U. S. P. 2,135,449 (1938) to D. J. Loder (to du Pont); U. S. P. 2,135,450 (1938) to A. T. Larson (to du Pont).
[104] U. S. P. 2,014,850 (1935) to Thomas Kane (to Edward Halford); British P. 398,527 (1933) to E. H. Strange and T. Kane; *C. A.*, 28, 1356.
[105] T. W. Edlund and K. R. Edlund, *Ind. Eng. Chem.*, 28, 1186-1188 (1936).

Auto-condensation of Ketones

When 150 cc of acetone is refluxed for four hours on the water-bath with sublimed aluminum chloride, condensation occurs with production of 15 cc of mesityl oxide [106]:



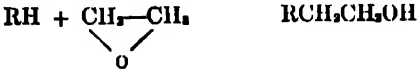
Upon further heating another mole of acetone adds to mesityl oxide with conversion to phorone,[107]

Hydration of Ethers; Dehydration of Alcohols

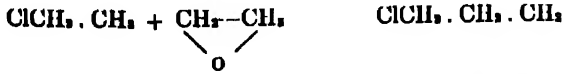
The hydration of aliphatic ethers to alcohols may be effected by subjecting an ether to hydration in the presence of aluminum chloride at elevated temperatures and a pressure in excess of 225 pounds per square inch.[108] Conversely, aluminum chloride may be used at 200-300° as a dehydrating agent in the production of ethers from alcohols.[109]

Alkylene Oxides with Hydrocarbons or Their Halogen Derivatives

Alcohols may be prepared by reaction of olefinic oxides with aliphatic or cycloaliphatic hydrocarbons or their halogen derivatives in the presence of aluminum chloride or other Friedel-Crafts type condensing agents.[110] Addition takes place according to the general scheme:



The hydrocarbon may be pentane, hexane, heptane, cyclohexane, or kerosene. Instead of ethylene oxide, other olefinic oxides, for example, propylene, butylene, or trimethylethylene oxide, may be used. With halogenated hydrocarbons, chlorohydrins are secured. Thus ethyl chloride and ethylene oxide in the presence of aluminum chloride yields 1,4-butylenechlorohydrin:



[106] J. G. Pereira, *Revista de la Real Academura de Ciencia de Madrid*, 7, 491 (1908); *Chemiker Z.*, 33, R 406 (1909). See also C. Courtot and V. Ouperoff, *Compt. rend.*, 191, 416-418 (1930), *C. A.*, 24, 5719, for auto-condensation of cyclohexanone, cyclopentanone, and cycloheptanone.

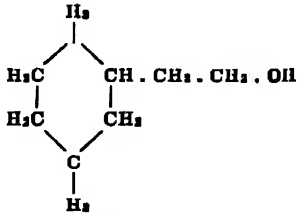
[107] E. Louis, *Compt. rend.*, 95, 602 (1882).

[108] U. S. P. 2,045,783 (1936) to W. K. Lewis (to Standard Oil Development Co.); Brit. P. 456,574 (1935) to Standard Oil Development Co., *Brit. Chem. Abs.*-B, 21 (1937).

[109] British P. 350,010 (1930) to N. V. de Bataafsche Petroleum Maats.; *Brit. Chem. Abs.*-B, 917 (1931).

[110] German P. 594,966 (1934) to H. Hopff (to I. G.), *C. A.*, 28, 5077; British P. 354,902 (1932) to I. G., *Brit. Chem. Abs.*-B, 13 (1933); French P. 716,604 (1931) to I. G., *C. A.*, 26, 2198.

When 500 parts of cyclohexane containing 132 parts of aluminum chloride are treated, with cooling and stirring, with 50 parts of ethylene oxide, there is obtained 70 parts of an oil (b.p. 95-105°/13 mm) which is composed mainly of hydroxyethylcyclohexane,



Treatment of a mixture of 500 parts of kerosene and 50 parts of aluminum chloride with ethylene oxide at 1.5 atmospheres and ordinary temperature until no further decrease of pressure is apparent results in production of 32 parts of an oil (b.p. 150-200°/12 mm) consisting mainly of higher alcohols.

Addition of Hydrogen Halides to Olefins

The formation of alkyl halides by the addition of hydrogen halides to olefins in the presence of catalysts has been studied quite extensively since the products of such reactions are of industrial importance. The reaction of ethylene and hydrogen chloride to form ethyl chloride is exothermic, and although the thermochemical data on the reaction are not in agreement, several workers [111] calculate the heat of formation as 20.7 calories. The two gases will not combine when heated, but in the presence of aluminum chloride and similar metal halide catalysts at 100-180° ethyl chloride is formed.[112] Propylene at 80° with aluminum chloride on silica gel gives isopropyl chloride in a 97 per cent yield. There is no indication of formation of *n*-propyl chloride, but a small amount of a higher-boiling compound, probably hexyl chloride, has been reported as a by-product of the reaction.[113]

The form of the catalyst is of importance; whereas aluminum chloride on asbestos or glass gives good results, pure aluminum chloride gives a mixture of hydrocarbons and organo-aluminum compounds.[114] The use of pressure permits lower temperatures.[115]

With ethyl chloride as solvent, the reaction of ethylene and hydrogen chloride in the presence of aluminum chloride at −78° gives a 99.7 per cent yield of ethyl chloride. Ethyl bromide can be prepared similarly.[116]

[111] C. Berthelot, *Ann. chim. phys. (5)*, 23, 238 (1881). E. Berl and J. Bitter, *Ber.*, 57, 95-99 (1924).
[112] E. Berl and J. Bitter, *loc. cit.* J. P. Wibaut, J. J. Diekmann, and A. J. Rutgers, *Rec. trav. chim.* 47, 477-495 (1928).
[113] L. G. Brouwer and J. P. Wibaut, *Rec. trav. chim.*, 53, 1001-1010 (1934); *C. A.*, 29, 447.
[114] J. P. Wibaut, *Z. Elektrochem.*, 35, 802-805 (1929).
[115] German P. 485,434 (1924) to I. G. (H. Suida, inventor); *C. A.*, 24, 886; U. S. P. 1,518,182 (1924), Can. P. 245,155 (1924) to G. O. Curme, Jr.; *C. A.*, 19, 522; U. S. P. 1,860,625 (1928) to W. R. Webb *C. A.*, 26, 51; U. S. P. 1,944,839 (1934) to E. B. Hjerpe and W. A. Gruse (to Gulf Refining Co.) *Brit. Chem. Abs.*-B, 928 (1934).
[116] A. J. Tulleners, M. C. Tuyn, and H. I. Waterman, *Rec. trav. chim.*, 53, 544-554 (1934); *C. A.*, 28, 4035.

This good yield can be obtained at somewhat higher temperatures, but as the temperature increases the conversion to polymeric products similarly increases; for example, at $-55°$ a 5 per cent residue was obtained, which increased to 11 per cent at $-12°$.[117]

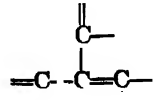
It is noteworthy that the aluminum chloride used in these experiments rapidly became deactivated, and that addition of aluminum prolonged the activity of the catalyst markedly. Whereas 1 g of aluminum chloride promoted the formation of 750 g of ethyl chloride before inactivation, in the presence of added aluminum the yield was increased to 5000 g of ethyl chloride.[118]

The use of ethyl chloride as solvent under pressure of 60 atmospheres has been claimed.[119] The use of a higher-boiling solvent such as trichloroethylene at 20-60° under atmospheric pressure permits the continuous removal of ethyl chloride, vaporization being effected by the heat of reaction.[120]

The production of alkyl halides may also be effected by passing a mixture of the olefin and hydrogen chloride through a solution of aluminum chloride in nitrobenzene, or by introducing ethylene into a current of hydrogen chloride containing aluminum chloride.[121]

An investigation dealing with the addition of hydrogen chloride to unsaturated hydrocarbons, using chlorides of bivalent, tervalent, and quadrivalent metals mounted on charcoal as catalysts, reveals optimum conditions for production of secondary chlorides. A hydrocarbon fraction containing 31 per cent amylene was treated with hydrogen chloride in the presence of catalysts for the production of amyl chlorides. It was found that passing the reactants through a tube at 70° followed by a second tube at 150° gave predominantly secondary chlorides, whereas the reversal of this order gave all possible chlorides. Moisture interfered with the formation of secondary chlorides.[122]

Leendertse [123] has studied the addition of hydrogen chloride to olefins from C_4 to C_{12} at a temperature of $-78°$. In general isoolefins in which the side-chain emanated from one of the carbon atoms of the olefin group, having the structure,



[117] D. M. Rudakovskii and A. G. Trifel, *Trans. expt'l Research Lab. "Khemgas." Materials on Cracking and Chem. Treatment of Cracking Products, U. S. S. R.* 3, 202-208 (1936); *C. A.*, 31, 5319 (1937).

[118] D. M. Rudakovskii, S. N. Alexandrov, V. K. Pashitnov, B. V. Ivanovski, and N. S. Golouschin, *Prom. Org. Chem.*, 4, 499-502 (1937); *Brit. Chem. Abs.-B*, 251 (1938)

[119] British P. 235,321 (1924) to Chemische Fabriken vorm Weiler-ter Meer; *C. A.*, 20, 918.

[120] British P. 466,184 (1936) to E. I. du Pont; *J. Inst. Petrol. Tech.*, 325A, (1937).

[121] French P. 780,057 (1935) to I. G. Farbenindustrie; *C. A.*, 29, 5862.

[122] W. J. Piotrowski and J. Winkler, *Przemysl Chem.*, 15, 25-36 (1931); *C. A.*, 25, 1794.

[123] J. J. Leendertse, *Rec. trav. chim.*, 57, (6), 796-797 (1938). J. J. Leendertse and H. I. Waterman, *Second World Petroleum Congress*, (1937), 2, (Sect. 2), 547-549; *J. Inst. Petr.*, 25, 205A (1939).

reacted rapidly to form the tertiary chloride without a catalyst; but olefins with a —C=C— structure were inert, and required a catalyst such as aluminum chloride for addition of hydrogen chloride. In the presence of aluminum chloride straight-chain olefins, with the exception of ethylene, yielded the normal monochlorides together with monochlorides of higher molecular weight products.

The addition of hydrogen chloride to diolefins such as butadiene and isoprene or rubber is promoted by aluminum chloride, with the formation of a white, spongy product.[124]

Reaction of Hydrogen Halides with Ethers or Alcohols

Alkyl halides may be prepared by reacting an aliphatic ether with an anhydrous halogen acid in the presence of aluminum chloride at a temperature below the boiling point of the alkyl halide.[125] The reaction may be effected by passing a mixture of ether vapor and halogen acid gas through a tower loosely packed with the catalyst. Or, the hydrogen halide gas may be passed through a stream of ether carrying the catalyst in suspension. Water which is evolved during the reaction eventually renders the metal salt inactive.

In another method,[126] condensation of ethyl ether with hydrogen chloride is effected by passing the reactants into contact with a bath of molten metal chlorides which are at a temperature in the range between about 125° and the decomposition point of ethyl chloride. When a mixture of ethyl ether and hydrogen chloride in a 1:2 ratio heated to 60° is continuously led into an $AlCl_3$-NaCl-$FeCl_3$ (60:30:10) bath held at 200°, there is obtained an 83 per cent of theoretical yield of ethyl chloride, based on the ether passed into the reaction bath.

The direct esterification of *tert*-butyl alcohol with hydrogen chloride for production of *tert*-butyl chloride occurs in the presence of aluminum chloride.[127]

In a study dealing with the alkylation of aromatic hydrocarbons with alcohols in the presence of aluminum chloride, it has been shown that conversion of alcohols into the corresponding alkyl halides occurs previous to alkylation. Thus, for example, in the presence of one mole of aluminum chloride isopropyl alcohol was converted into isopropyl chloride in a 70 per cent yield.*

Addition of Hydrogen Halides to Olefinic Halides

1,1-Dichloroethane may be prepared in a 20-40 per cent yield by passing vinyl chloride and hydrogen chloride over aluminum chloride at 125°; only a small amount of 1,2-dichloroethane is formed as by-product.[128]

[124] British P. 447,110 (1936) to Marsens Corp. of America.
[125] U. S. P. 2,015,706 (1935) to B. T. Brooks (to Standard Alcohol Co.).
[126] U. S. P. 2,140,800 (1938) to J. L. Amos (to Dow Chemical Co.).
[127] U. S. P. 2,012,732 (1935) to W. V. Wirth (to E. I. du Pont); *C. Z.*, 1936 I, 2826.
* See page 617.
[128] U. S. P. 1,900,276 (1933) to G. H. Coleman (to Dow Chemical Co.).

An optional method of preparation involves the passage of the same reactants into a chlorinated solvent such as trichloroethane, acetylene tetrachloride, or preferably 1,1-dichloroethane containing aluminum chloride in suspension at about 0°. The yield is claimed to be almost quantitative.[129] In the presence of not more than 6 per cent of aluminum chloride, based on the vinyl chloride, and with an excess of hydrogen chloride, temperatures of 15-60° may be used.[130]

The addition of hydrogen chloride to *sym*-dichloroethylene containing 5 to 10 per cent of aluminum chloride at 30-40° gives a good yield of 1,1,2-trichloroethane; trichloroethylene similarly yields 1,1,1,2-tetrachloroethane.[131] This is in accordance with the Markownikoff rule. Hydrogen bromide adds on similarly to form 1,1,2-trichloro-1-bromoethane, although in the presence of air or oxidizing agents instead of aluminum chloride, the peroxide effect is evident in that the product is 1,1,2-trichloro-2-bromoethane.[132] Reaction of 1,1-dichloro-1-propene with hydrogen chloride in the presence of aluminum chloride yields 1,1,1-trichloropropane.[133]

Halogenation

Halogenation of unsaturated hydrocarbons, particularly olefins such as ethylene or propylene, is promoted by the use of a catalyst comprising a complex cyanide and aluminum chloride. The catalyst may be prepared by evaporating an aqueous solution of an alkali or alkaline earth metal ferrocyanide or cuprocyanide and aluminum chloride.[134] 1,2-Dichloroethane is formed by passing ethylene together with the amount of chlorine required for the catalyst at temperatures below 250°. Steam was found to promote the addition reaction and inhibit substitution.

Ethylene polymers with a molecular weight of 2,000 to 24,000 either in the molten state or preferably in an inert solvent may be halogenated, using aluminum chloride as a catalyst, to produce horn-like, rubber-like, or fibrous products which are useful for electrical insulation.[135]

The chlorination of acetylene in the absence of catalysts occurs with explosive violence. According to Mouneyrat,[136] the reaction may be effected in presence of aluminum chloride; in recent practice, however, other catalysts have been used. The halogenation of nonbenzenoid polymerides of acetylene with sulfuryl chloride may be effected at 30-35° in the presence of aluminum chloride to give a dichlorohexatriene.[137]

Saturated aliphatic hydrocarbons can also be chlorinated in the pres-

[129] British P. 454,128 (1936), *Brit. Chem. Abs.*-B, 1192 (1936); French P. 801,490 (1936), *C. A.*, 31, 420, to Consortium für Elektrochem. Ind. G. m. b. H.
[130] U. S. P. 2,007,144 (1935) to H. S. Nutting, P. S. Petrie, and M. E. Huscher (to Dow Chem. Co.).
[131] H. J. Prins, *Rec. trav. chim.*, 45, 80-81 (1926); *C. Z.*, 1926 II, 151.
[132] M. S. Kharasch, J. A. Norton, and A. F. B. Mayo, *J. Organic Chem.*, 3, 43-54 (1938).
[133] British P. 503,615 (1939) to A. A. Levine and O. W. Cass (to E. I. du Pont); *C. A.*, 33, 6872.
[134] British P. 449,411 (1935), *Brit. Chem. Abs.*-B, 919 (1936); French P. 801,395 (1936), *C. A.*, 31, 416; German P. 660,642 (1938), *C. A.*, 32, 666 to N. V. de Bataafsche Petroleum Maats. U. S. P. 2,043,932 (1936) to A. F. A. Reynhart (to Shell Development Co.).
[135] British P. 481,515 (1936) to E. W. Fawcett (to Imperial Chemical Ind.).
[136] A. Mouneyrat, *Compt. rend.*, 126, 1805-1808 (1898); *J. Chem. Soc. Abs.*, 74 (I), 613 (1898).
[137] U. S. P. 1,990,160 (1935) to W. S. Calcott and A. S. Carter (to E. I. du Pont); *Brit. Chem. Abs.*-B, 984 (1935).

ence of aluminum chloride. Products such as tetrachloroethane may be prepared using a molten $AlCl_3$-$FeCl_3$-NaCl catalyst at 250-500°.[138]

The chlorination of hexane fractions with or without a solvent with aluminum chloride as a catalyst gives heptachlorohexane, $C_6H_7Cl_7$, which is a useful cleaning solvent.[139]

Chlorination of aliphatic acids with production of the corresponding acid chlorides may be conducted by treating the acid with a double compound of sulfur tetrachloride and aluminum chloride, produced by passing chlorine into sulfur dichloride and aluminum chloride.[140]

The halogenation of compounds containing an abietyl group has been claimed to proceed favorably if the reaction is conducted in the presence of aluminum chloride.[141]

Chlorination of acetyl derivatives of sugars by treatment with phosphorus pentachloride is catalyzed by aluminum chloride.[142] If a highly reactive aluminum chloride is employed in excess, however, chlorination is effected in the absence of the pentachloride, the aluminum chloride serving as halogenating agent. Chlorination of lactose octa-acetate occurs upon treatment of 100 g of the latter dissolved in chloroform with 200 g of aluminum chloride at 65° for two hours.[143] The method has also been applied to the chlorination of cellobiose octa-acetate.[144]

The use of aluminum chloride as a catalyst for halogenation of partially halogenated hydrocarbons has long been known. Tawildaroff [145] observed that the action of chlorine on ethylidene chloride in the presence of aluminum chloride produces only trichloroethane (b.p. 114°), the halogen attacking only the group which does not already contain chlorine. Subsequently Mouneyrat [146] found that temperature has a decided influence on the chlorination of *sym*-dichloroethane in the presence of aluminum chloride. At 100° halogen was scarcely, if at all, absorbed; but at 118-120°, the formation of hexachloroethane occurred.

1,1,2-Trichloroethane is prepared by passing chlorine and ethylene chloride, in the ratio of between about 0.55 and about 0.75 part by weight of chlorine per part of ethylene chloride, into a bath of molten metal chlorides maintained at a temperature between about 300-425°. Using a bath consisting of 36 parts by weight of potassium chloride and 64 parts by weight of aluminum chloride at 350°, a 64 per cent of theoretical yield of 1,1,2-trichloroethane was secured.[146]

The production of hexachloroethane from perchloroethylene by reac-

[138] U. S. P. 2,084,282 (1935) to J. J. Grebe, J. H. Reilly, and R. M. Wiley (to Dow Chemical Co.); *C. A.*, **30**, 5178.
[139] British P. 286,726 (1928) to F. S. Vivas; *Brit. Chem. Abs.*-B, 349 (1929). French P. 650,735 (1928) to International Fireproof Products Corp.; *C. A.*, **23**, 3341.
[140] U. S. P. 1,805,162 (1931) to E. C. Britton (to Dow Chemical Co.); *Brit. Chem. Abs.*-B, 494 (1932).
[141] U. S. P. 2,050,979 (1936) to Hercules Powder Co.; *C. A.*, **30**, 6763.
[142] F. v. Arlt, *Monatsh.*, **22**, 144-150 (1901), *J. Chem. Soc. Abs.*, 1901 I, 369. H. Skraup and R. Kremann, *Monatsh.*, **22**, 575-584 (1901).
[143] A. Kunz and C. S. Hudson, *J. Am. Chem. Soc.*, **48**, 1978-1984 (1926).
[144] C. S. Hudson, *J. Am. Chem. Soc.*, **48**, 2002-2004 (1926).
[145] N. I. Tawildaroff, *Bull. soc. chim. (2)*, **34**, 546; *J. Chem. Soc. Abs.*, 398 (1881).
[146] U. S. P. 2,140,549 (1938) to J. H. Reilly (to Dow Chemical Co.).

tion with chlorine in the substantial absence of light and in the presence of aluminum chloride has been claimed.[147]

The further chlorination of polyvinyl chloride with elemental chlorine may be effected in the presence of aluminum chloride.[148]

Reaction of Chlorinated Paraffins or Olefins with Olefinic Chlorides

Much work has been done on the reaction of chlorinated paraffins with chlorinated olefins in the presence of aluminum chloride. In 1911, Böeseken and Prins[149] announced that heptachloropropane is formed by heating tetrachloroethylene in an excess of chloroform in the presence of aluminum chloride:

$$CHCl_3 + Cl_2C{:}CCl_2 \qquad CHCl_2CCl_2.CCl_3$$

The following condensations took place in the same way[150]:

$$CCl_2{:}CHCl + CHCl_3 \rightarrow CCl_3.CHCl.CHCl_2$$
$$CCl_2{:}CHCl + CCl_4 \rightarrow CCl_3.CHCl.CCl_3$$
$$CHCl{:}CHCl + CCl_4 \rightarrow CCl_3.CHCl.CHCl_2$$
$$CHCl{\cdot}CHCl + CHCl_3 \longrightarrow CHCl_2.CHCl.CHCl_2$$

Also,

$$CHCl_2CCl_3 + CHCl_3 \rightarrow CHCl_2.CCl_2.CCl_3 + HCl$$

No indication of the formation of intermediate products was found. It was assumed that the aluminum chloride renders the chlorinated paraffin active, so that its molecular components attach themselves to the double linking of the chlorinated olefin, which has also been activated with the aluminum chloride.

asym-Heptachloropropane has been prepared in an 88-93 per cent of theoretical yield by refluxing gently for 15 hours a mixture consisting of 166 g of tetrachloroethylene, 300 g of dry chloroform, and 27 g of aluminum chloride, cooling the product to room temperature and decomposing with ice. Fractionation of the organic layer at atmospheric pressure removes unreacted chloroform, and the heptachloropropane is secured by distillation at diminished pressure.[151] Henne and Ladd[152] report that they secured 6.8 moles of *asym*-heptachloropropane by refluxing during 20 hours 10 moles of tetrachloroethylene, 20 moles of chloroform, and 50 g of aluminum chloride. These investigators also prepared *sym*-heptachloropropane, $CCl_3.CHCl.CCl_3$, in a 49 per cent yield by heating 520 g of trichloroethylene with 1220 g of carbon tetrachloride and 50 g of aluminum chloride at 20-30° for 48 hours.

[147] U. S. P. 2,087,419 (1936) to A. Levine and H. A. Bond (to E. I. du Pont); *C. A.*, 30, 3837.
[148] French P. 46,675 (1936) to I. G. Farbenindustrie; *C. A.*, 31, 8067 (1937).
[149] J. Böeseken and H. J. Prins, *K. Akad. Wetenschappen*, 19, 776-778 (1911); *C. A.*, 5, 2845; *C. Z.*, 1911 I, 466.
[150] J. Böeseken and H. J. Prins, *K. Akad. Wetenschappen*, 13, 685-687 (1911); *J. Chem. Soc. Abs.* (I), 173 (1911). J. Böeseken, *Rec. trav. chim.*, 30, 148-150 (1911); *C. A.*, 5, 3400. H. J. Prins, *J. prakt. Chem.*, 89, 414-424, 425-451 (1914); *J. Chem. Soc. Abs.*, 106 (I), 648 (1914). German P. 261,689 (1913) to H. J. Prins; *C. A.*, 1913 II, 394.
[151] M. W. Farlow, *Org. Syntheses*, 17, 58-59 (1937).
[152] A. L. Henne and E. C. Ladd, *J. Am. Chem. Soc.*, 60, 2491-2495 (1938).

The condensation of dichloroethylene with chloroform, effected by heating the reactants at 50° for two hours, gives a 70 per cent yield of 1,1,2,3,3-pentachloropropane.[153]

The production of polychloro-paraffins by addition of a chlorinated paraffin to an olefinic halide has been shown to be a reversible reaction only at lower temperatures.[154] Heptachloropropane, $CCl_3.CCl_2.CHCl_2$, is decomposed by aluminum chloride into chloroform and tetrachloroethylene:

$$CCl_3 . CCl_2 . CHCl_2 \xrightarrow{AlCl_3} CHCl_3 + CCl_2 : CCl_2$$

At 80°, the vapor pressure, which should reach a limit, increases continually because of the formation of hydrogen chloride; a decomposition of the heptachloropropane to hexachloropropene and hydrogen chloride occurs. A thorough study of the effect of temperature showed that aluminum chloride is active at a temperature at which the equilibrium in the equation given above is far to the left, and at which the decomposition into hydrogen chloride and hexachloropropene is of secondary importance The formation of heptachloropropane from tetrachloroethylene and excess of chloroform is initiated at about 65°. Higher temperatures are required if less aluminum chloride is used. An increase of temperature accelerates it very markedly, but at the same time the decomposition of the product with cleavage of hydrogen chloride appears, so that at 108°, less of the heptachloropropane is formed than at 100°. At 130° 90.5 per cent of the decomposition is according to

$$CCl_3 . CCl_2 . CHCl_2 \qquad CCl_3 . CCl : CCl_2 + HCl$$

Since the foregoing reaction is not reversible, the preparation of heptachloropropane is best effected by using an excess of chloroform and as low a temperature as possible.

Synthesis of polychlorinated olefins from lower polychlorinated paraffins may be effected by combining the Prins reaction with dehydrohalogenation. Thus, when pentachloroethane is heated with 1.5 per cent of its weight of aluminum chloride for 1½ hours at 100-110°, a 95 per cent yield of tetrachloroethylene is secured:

$$CHCl_2 . CCl_3 \xrightarrow{AlCl_3} CCl_2 : CCl_2 + HCl$$

When the tetrachloroethylene is boiled for ten minutes with chloroform which had been freshly distilled over 0.5-1 per cent of aluminum chloride, asymmetric heptachloropropane is formed:

$$CCl_2 : CCl_2 + CHCl_3 \qquad CHCl_2 . CCl_2 . CCl_3$$

[153] H. J. Prins and J. W. Engelhard, *Rec. trav. chim.*, 54, 307 (1935).
[154] J. Böeseken, J. van der Scheer, and J. G. de Voogt, *Rec. trav. chim.*, 34, 78-95 (1915); *C. A.*, 9, 1756.

A chloroform solution of the latter heated with aluminum chloride to 60-70° until evolution of hydrogen chloride has ceased gives an 83 per cent yield of hexachloropropene [155]:

$$CHCl_2 . CCl_2 . CCl_3 \qquad CCl_2 : CCl . CCl_3 + HCl$$

The addition of chlorinated paraffins to olefinic chlorides in the presence of aluminum chloride is not of general applicability.[156] Mono- and dichloromethane have been found to give no reaction. With the olefins, the reaction velocity was found to increase from tetrachloro- to monochloroethylene. Ethylene, itself, however, did not enter into the reaction, even with highly activated chloro-compounds. Certain chloroethanes can also add to chloroethylenes, the reaction velocity, however, being slower than that with the chloromethanes. Chloropropanes do not react with chloroethylenes, except pentachloropropane. Chloropropenes, as well as other unsaturated chlorocompounds with a CCl_3 or CCl_2 group vicinal to the double bond react in the normal way.

Reactions of chloroethanes with chloro-olefins in the presence of aluminum chloride have been investigated by Prins.[157] Condensations with 1,2-dichloroethane give only small amounts of resins, hexachloroethane does not react, and *sym*-tetrachlorethane gives no condensation products. Under the influence of aluminum chloride, the chloroethanes split out hydrogen chloride, forming unsaturated compounds which resinify. However, 1,2,2-trichloroethane adds to 1,2-dichloroethylene when equal quantities of the reactants are treated with 1 per cent of dry aluminum chloride and the reaction mixture is kept at 35-40° for 5 days to give a 50 per cent yield of crude 1,2,3,4,4-pentachlorobutane:

$$CH_2Cl . CHCl_2 + CHCl : CHCl \longrightarrow CH_2Cl . CHCl . CHCl . CHCl_2$$

The condensation of 1,1-dichloroethane with a chloroethylene for production of chlorobutanes has been claimed.[158] Reaction is effected in the presence of aluminum chloride, preferably at below 60°, and with an excess of the chlorinated paraffin. The olefinic halide may be vinyl chloride, *sym*-dichloroethylene, or trichloroethylene.

An attempt has been made to extend the reaction to the condensation of one chloro-olefin with another. Hexachloropropene and aluminum chloride at 80° form a crystalline additive compound which reacts vigorously with *sym*-dichloroethylene, but the only product obtained was a compound formed by reaction of 3 moles of dichloroethylene. On the other hand, reaction in dichloromethane at 5-6° gives a good yield of the expected octachloropentene.[159]

Upon reacting hexachloropropene with trichloroethylene and aluminum

[155] H. J. Prins, *Rec. trav. chim.*, 54, 249-252 (1935); *C. A.*, 29, 3298.
[156] H. J. Prins, *Rec. trav. chim.*, 51, 1065-1080 (1932); *C. A.*, 27, 480.
[157] H. J. Prins, *Rec. trav. chim.*, 56, 119-125 (1937); *C. A.*, 31, 2009.
[158] British P. 453,414 (1936); French P. 806,878 (1936) to Consortium für elektrochemische Industrie; *C. A.*, 31, 1046, 4677.
[159] H. J. Prins, *Rec. trav. chim.*, 56, 779-784 (1937); *Brit. Chem. Abs.*-A (II), 488 (1937).

chloride, however, Prins [160] reported an 82 per cent of theoretical yield of nonachloropentene. Dodecachloroheptene is also formed, probably by the reaction of the nonachloropentene formed with additional trichloroethylene. The condensation may be effected in either dichloromethane or chloroform as diluent. Although chloroform is able to condense with trichloroethylene, it does not interfere in the reaction because of its low reaction velocity, and because the reaction is so conducted as to effect a firm binding of the catalyst with one of the reactants.

Metathetical Reactions between Halogenated Aliphatic Compounds

Metathetical reactions occur between certain types of aliphatic halogen compounds in the presence of aluminum chloride. Chloroform and ethyl bromide with aluminum chloride at room temperature give ethyl chloride and about 35 per cent of monobromodichloromethane:

$$CHCl_3 + C_2H_5Br \xrightarrow{AlCl_3} C_2H_5Cl + CHCl_2Br$$

1,2-Dichloroethane and 1,2-dibromoethane enter into the same type of reaction. After 35 hours at 25°, monochloromonobromoethane is formed.[161]

Treatment of *sym*-tetrachloroethane with bromine at 105° in the presence of aluminum chloride results in the production of dichlorodibromoethane, CHClBr.CHClBr, and a trichlorotribromoethane for which the structure $CCl_2Br.CBr_2Cl$ was assumed.[162]

According to Henne and Newman, Prins' method for the preparation of polyhalogenated paraffins cannot be extended to the condensation of fluorinated molecules of methane and ethylene, probably because organically bound fluorine is replaced by chlorine in the presence of aluminum chloride.[163] This replacement of fluorine by chlorine may be seen in the production of difluorochloromethane and chloroform by treatment of dichlorofluoromethane with aluminum chloride under reflux at about atmospheric pressure at temperatures of 8-25°.

$$2CHCl_2F \xrightarrow{AlCl_3} CHClF_2 + CHCl_3$$

In the same way, chlorine replaces fluorine when trichloromonofluoromethane gives carbon tetrachloride and difluorodichloromethane:

$$2CCl_3F \xrightarrow{AlCl_3} CCl_2F_2 + CCl_4$$

A fluorine atom of one molecule is thus substituted by a chlorine atom of another molecule.[164]

[160] H. J. Prins, *Rec. trav. chim.*, **57**, 659-666 (1938)
[161] G. Dougherty, *J. Am. Chem. Soc.*, **51**, 576-580 (1929); *C. A.*, **23**, 1399.
[162] A. Mouneyrat, *Compt. rend.*, **126**, 1805-1808 (1898); *J. Chem. Soc. Abs*, **74** (I), 613 (1898).
[163] A. L. Henne and M. S. Newman, *J. Am. Chem. Soc.*, **60**, 1697-1698 (1938).
[164] U. S. P. 1,994,035 (1935) to C. W. Croco (to Kinetic Chemicals, Inc.); *C. A.*, **29**, 2974, for like conversion of $CF_2Cl.CCl_2F$ into $CF_2Cl.CCl_3$, see W. T. Miller, *J. Am. Chem. Soc.*, **62**, 998 (1940).

Halogen exchange also occurs when ethyl iodide is reacted with chloroform and aluminum chloride in the molecular ratio 3:1:0.07. An almost quantitative yield of iodoform is secured.

$$3C_2H_5I + CHCl_3 \xrightarrow{AlCl_3} 3C_2H_5Cl + CHI_3$$

Analogously, ethyl iodide with carbon tetrachloride yields carbon tetraiodide.[165]

Methyl iodide with ethyl bromide and ethylene dibromide with ethyl iodide similarly undergo exchange reactions[161]:

$$CH_3I + C_2H_5Br \xrightarrow{AlCl_3} CH_3Br + C_2H_5I$$

$$C_2H_4Br_2 + 2C_2H_5I \xrightarrow{AlCl_3} 2C_2H_5Br + C_2H_4I_2$$

Redistribution has been found to occur between ethylene dichloride and dibromide, between ethyl chloride and ethylene dibromide, and between ethyl bromide and ethylene dichloride in the presence of 1.5-3 mole per cent of aluminum chloride as the catalyst.[166]

Cleavage of Hydrogen Halides

In the preceding discussion of the preparation of polychloro- hydrocarbons, it has been pointed out that under certain conditions aluminum chloride effects dehydrohalogenation of halogenated compounds. In 1885, Kerez[167] reported that by heating propyl iodide with aluminum chloride at 110-168°, a 75 per cent yield of propylene was secured. Propyl bromide and propyl chloride likewise were observed to decompose with formation of propylene and the corresponding hydrogen halides. No formation of propane was observed with any of the halides. A few years later, however, Meyer[168] reported that when primary, secondary, or tertiary iodides were heated with aluminum chloride in a closed tube, only paraffins were formed, although reaction in an open vessel yields olefins. In

-iodide	Temp. (°C)	Product
Isopropyl	145	propane
n-Butyl	140	butane
sec-Butyl	80	butane
sec-Butyl	160	propane
sec-Butyl	225	propane
tert-Butyl	30	butane
tert-Butyl	140	propane and butane
tert-Butyl	150	propane
Isoamyl	140	butane
sec-n-Hexyl	80	hexane
sec-n-Hexyl	90	hexane and butane
sec-n-Hexyl	128	butane and propane
sec-n-Hexyl	225	propane
sec-Octyl	125	butane

[165] J. W. Walker, *J. Chem. Soc.*, **85**, 1082-1098 (1904).
[166] G. Calingaert, H. Soroos, V. Hnizda, and H. Shapiro, *J. Am. Chem. Soc.*, **62**, 1545-1547 (1940).
[167] C. Kerez, *Ann.*, **231**, 285-307 (1885); *J. Chem. Soc. Abs.*, **50**, 435 (1886).
[168] L. Meyer, *Ber.*, **27**, 2766-2767 (1894); *J. Chem. Soc. Abs.*, **68** (I), 2 (1895).

a closed tube at 130°, propyl iodide with aluminum chloride gave propane Other alkyl iodides also yielded saturated hydrocarbons at the temperatures shown on preceding page.

Here the cracking of the primarily formed hydrocarbons is apparent at higher temperatures.

In recent years, dehydrohalogenation of alkyl halides, for production of olefins, has been generally effected with catalysts other than aluminum chloride. On the other hand, dehydrohalogenation of polychloro- aliphatic hydrocarbons is commonly effected in the presence of aluminum chloride.

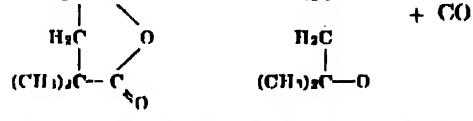
Mouneyrat [169] observed that when ethylene dichloride is heated under reflux with aluminum chloride at 70-75°, it decomposed into acetylene and hydrogen chloride. As has been already mentioned in studying the mechanism of the formation of *asym*-heptachloropropane from chloroform and *sym*-tetrachloroethane, Böeseken and his co-workers [170] noted that at 130° 90.5 per cent of the heptachloropropane formed decomposes into hexachloropropene and hydrogen chloride Prins [171] secured a 95 per cent yield of tetrachlorethylene by heating pentachloroethane for 1½ hours at 100-110° with 1.5 per cent of its weight of aluminum chloride A continuous method for the production of perchloroethylene from pentachloroethane has been recently described.[172] Pentachloroethane is added continuously to a boiling mixture of perchloroethylene and about 3 per cent by weight of aluminum chloride, contained in the lower part of a fractionating column so that the perchloroethylene formed is immediately fractionated off.

It has been claimed that the compound C_4HCl_5, presumably pentachlorobutadiene, is secured upon heating hexachlorobutene with aluminum chloride.[173]

Decomposition of Oxygenated Aliphatic Compounds

There are isolated citations in the literature of other examples of the decomposing effect on aliphatic compounds.

The action of aluminum chloride on anhydrides of some aliphatic dicarboxylic acids results in evolution of carbon monoxide and formation of lactones and a mixture of saturated dicarboxylic and unsaturated mono-carboxylic acids.[174] α,α-Dimethylglutaric anhydride thus yields isohexolactone:

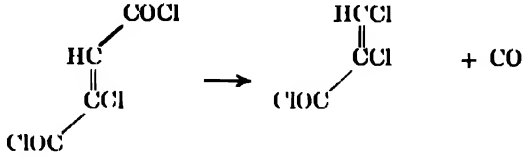


[169] A. Mouneyrat, *Compt. rend.*, 126, 1805-1808 (1898); *Bull soc. chim. (3)*, 19, 446
[170] J. Böeseken, J. van der Scheer, and J. G. de Voogt, *Rec. trav chim.*, 34, 78-95 (1915) (
9, 1765.
[171] H. J. Prins, *Rec. trav. chim.*, 54, 249-252 (1935); *C. A.*, 29, 3298.
[172] British P. 500,176 (1939) to Consortium für Elektrochemische Industrie; *C. Z.*, 1939 I, 3709
[173] Brit. P. 502,061 (1939) to Consortium fur Elektrochemische Industrie.
[174] M. Desfontaines, *Compt. rend.*, 134, 793-796 (1902), *J. Chem. Soc. Abs.*, 82 (I), 258 (1902)

At the same time, α,α-dimethylglutaric and pyroterebic acids are formed. Dimethylsuccinic anhydride yields carbon monoxide, dimethylacrylic acid, and dimethylsuccinic acid.

When camphoric anhydride in chloroform solution is treated with aluminum chloride, carbon monoxide is given off, with formation of isolauronolic acid and a mixture of isomeric lactones.[175]

Chlorides of dicarboxylic acids may decompose with evolution of carbon monoxide upon heating with aluminum chloride. Chlorofumaric acid chloride thus yields α,β-dichloroacrylyl chloride [176]:



Chloral also decomposes with cleavage of carbon monoxide when heated with aluminum chloride.[177] The decomposing effect of aluminum chloride on aliphatic aldehydes may be indicated by the fact that diaryl paraffins are obtained in Friedel-Crafts reaction of the aldehydes with aromatic hydrocarbons.[178]

The action of aluminum chloride on methyl, ethyl, or propyltrichloromethyl carbonate results in cleavage, with production of carbon dioxide, phosgene, and the corresponding alkyl chloride.[179]

When esters of tetraethylsuccinic acid are treated with aluminum chloride at 200°, decomposition occurs, with evolution of alkyl chloride and tetraethylsuccinic anhydride. The latter can be separated from aluminum chloride without loss by distillation at 270°. This affords a good method for production of anhydrides from esters whose saponification is prevented by steric hindrance.[180]

A method for the production of dichloroacetyl chloride and chloral is based on the decomposing effect of aluminum chloride. Trichloroethylene is oxidized by oxygen at room temperature to an oxide. Upon treatment with aluminum chloride the oxidation product is converted into a mixture of dichloroacetyl chloride and chloral.[181]

A process for manufacture of alkyl chlorides consists of decomposing alkyl chlorosulfites in the presence of aluminum chloride.[182]

[175] E. Bureker, *Compt. rend.*, 119, 426 (1894); *Bull. soc. chim. (3)*, 13, 901 (1895). G. Blanc, *Compt. rend.*, 123, 749 (1896); 124, 468 (1896); 129, 1019-1020 (1899); *J. Chem. Soc. Abs.*, 78 (I), 133 (1900); *Bull. soc. chim. (3)*, 15, 1191 (1896); *(3)*, 23, 893-895 (1900); *J. Chem. Soc. Abs.*, 78 (I), 586 (1900). F. H. Lees and W. H. Perkin, Jr., *J. Chem. Soc.*, 79, 332-361 (1901). W. H. Perkin, Jr. and J. Yates, *J. Chem. Soc.*, 79, 1378-1396 (1901).

[176] E. Ott, *Ann.*, 392, 245-255 (1912).

[177] J. Böeseken, *Rec. trav. chim.*, 30, 381-391 (1911); *C. A.*, 6, 623. J. Böeseken and A. Schimmel, *Rec. trav. chim.*, 32, 128-135 (1913); *J. Chem. Soc. Abs.*, 104 (I), 828 (1913).

[178] J. Böeseken, *loc. cit.* K. Bodendorf, *J. prakt. Chem. (2)*, 129, 337-339 (1931); *Brit. Chem. Abs.-A*, 604 (1931).

[179] N. N. Melnikov, *J. Russ. Phys.-Chem. Soc.*, 62, 2019-2022 (1930); *C. A.*, 25, 4228.

[180] E. Ott, *Ber.*, 70, 2362 (1937); *C. A.*, 32, 1242 (1938).

[181] British P. 353,099 (1930) to Consortium für Elektrochem. Ind.; *Brit. Chem. Abs.-B*, 332 (1931).

[182] Russian P. 51,419 (1937) to Ya. L. Gol'dfarb and L. M. Smorgonskii; *C. A.*, 35, 6877.

Betulin, abietic acid, and American colophony are converted into optically active hydrocarbons upon heating with aluminum chloride.[183]

Brus [184] discloses the preparation of hydrocarbon oils by the catalytic cracking of resins such as colophony, tar, etc. Benzene- and benzene-like hydrocarbons were obtained, together with solid hydrocarbons such as naphthalene, anthracene, and phenanthrene.

Zelinskii and Lavrovski [185] have studied the reaction of such substances as cholesterol, oleic, palmitic, and stearic acids with aluminum chloride with a view to elucidation of the source of petroleum. When mixtures of these liquids with aluminum chloride are heated, gaseous, liquid, and solid products are obtained which have many similarities to crude petroleum. The authors conclude that palmitic and stearic acids may very well be the mother substance of the paraffin-rich petroleums.

The liquid-phase cracking of vegetable oils in the presence of 1 per cent by weight of anhydrous aluminum chloride has been described.[186] Using cottonseed, castor, perilla, soybean, tung, sesame, linseed, hempseed, and peanut oils, 34-46 per cent of oil distilling below 250° was obtained.

Aliphatic Reactions with Compounds of Arsenic, Phosphorus, Nitrogen, and Sulfur

Arsenic.—In 1904, Nieuwland [187] reported that when aluminum chloride is added to a mixture of arsenic trichloride and acetylene, reaction occurred with the formation of material which gave off noxious fumes. Subsequently Dafert [188] noted that at ordinary temperatures the reaction yielded a product which he designated as diacetylene arsenic trichloride, $AsCl_3,2C_2H_2$, and at higher temperatures a black, organic-arsenic compound of high molecular weight. Upon passing acetylene for six hours into a carbon tetrachloride solution of 440 g of arsenic trichloride and 300 g of aluminum chloride, and keeping the temperature below 15°, Green and Price [189] noted the formation of three compounds, (β-chlorovinyl) dichloroarsine, bis-(β-chlorovinyl) chloroarsine, and tris-(β-chlorovinyl) arsine, the last being the main product. Use of a limited amount of acetylene resulted in formation of only the secondary and tertiary arsines, a considerable part of the arsenic trichloride being recovered unchanged The production of the three arsines occurs through addition of arsenic halide at the acetylenic bond:

[183] N. D. Zelinski and N. S. Kozlov, *Ber.*, 64, 2130-2135 (1931); *Brit. Chem. Abs.*-A, 1299 (1931).
[184] French P. 810,037 (1937) to G. Brus; *C. Z.*, 1937 II, 1394.
[185] N. D. Zelinskii and K. P. Lavrovski, *Ber.*, 61, 1054-1057 (1928); *C. A.*, 22, 2920; cf. also *C. A.*, 22, 89. For the formation of saturated and unsaturated hydrocarbons by treatment of aliphatic esters with $AlCl_3$, see H. Gault and E. Beloff, *Bull. soc. chim.*, 5, 295-304 (1938).
[186] K. Ping, *J. Chinese Chem. Soc.*, 3, 281-287 (1935); *Brit. Chem. Abs.*-B, 980 (1935). See also J. Banson, *Philippine Agr.*, 25, 817-832 (1937); *C. A.*, 31, 4818, for $AlCl_3$ cracking of cocoanut oil to give hydrocarbons.
[187] J. A. Nieuland, Dissertation, Notre Dame, 1904, 152 pp.
[188] O. A. Dafert, *Monatsh.*, 40, 313-323 (1919); *J. Chem. Soc. Abs.*, 118 (I), 18 (1920).
[189] S. J. Green and T. S. Price, *J. Chem. Soc.*, 119, 448-453 (1921).

$$3CH \vdots CH + AsCl_3 \xrightarrow{AlCl_3} (CHCl : CH)_3As$$

$$2CH \vdots CH + AsCl_3 \xrightarrow{AlCl_3} (CHCl : CH)_2AsCl$$

$$CH \vdots CH + AsCl_3 \xrightarrow{AlCl_3} CHCl : CH . AsCl$$

It was shown that tris-(β-chlorovinyl)arsine, usually the main product, can be converted quantitatively to a mixture of the primary and secondary chloroarsines by heating at 200-250° with arsenic trichloride:

$$(CHCl : CH)_3As + 2AsCl_3 \longrightarrow 3CHCl : CH . AsCl_2$$

$$2(CHCl : CH)_3As + AsCl_3 \longrightarrow 3(CHCl : CH)_2AsCl$$

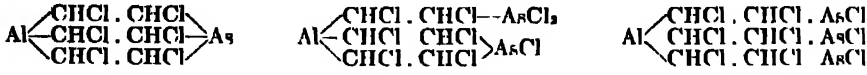
The preparation of chlorovinylarsines was further studied by Mann and Pope,[190] who made a more thorough examination of the properties of the three products. Wieland and Bloemer [191] account for the formation of all three products by postulating a mechanism involving the primary formation of (β-chlorovinyl)dichloroarsine, its reaction with a second molecule of acetylene to give bis(β-chlorovinyl)chloroarsine, and subsequent combination of this secondary arsine chloride with a further molecule of acetylene to give the trisubstituted arsine.

A comprehensive study of the reaction has been made by Lewis and Perkins.[192] These investigators worked out optimum conditions which are illustrated in the following typical run: Arsenic trichloride (35 moles) was treated with 0.25 mole of aluminum chloride in a two-gallon autoclave, and acetylene was introduced for 2½ hours at an initial temperature of 24° and an average of 42°, the maximum temperature being 45°. During this time the absorption of acetylene fell from 0.48 cubic feet per minute to 0.06, the total absorbed being 30 cubic feet (909 g), or 1 mole per mole of arsenic trichloride. Unless precautions are taken, explosions occur during distillation. It was found that these could be avoided by washing the reaction mixture with 20 per cent hydrochloric acid, instead of hydrolyzing the product according to ordinary Friedel-Crafts procedure. Hydrochloric acid of this strength extracted the aluminum chloride and left a product which generally showed no explosive tendency. Flash distillation of the washed material gave a 74.2 per cent yield of organic matter, based on the original arsenic trichloride. Of this, 74.3 per cent was (β-chlorovinyl)dichloroarsine.

This primary arsine is known in gas warfare as Lewisite. It is a strong vesicant and respiratory irritant. The secondary arsine, bis-(β-chlorovinyl)chloroarsine, does not have as powerful a vesicating action, but is more irritating. tris-(β-Chlorovinyl)arsine is almost without action on the skin.

[190] F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 121, 1754-1759 (1922).
[191] H. Wieland and A. Bloemer, *Ann.*, 431, 34-39 (1923), *J. Chem. Soc. Abs.*, 124 (I), 490 (1923).
[192] W. L. Lewis and G. A. Perkins, *Ind. Eng. Chem.*, 15, 290-295 (1923).

Lewis and Perkin proposed that the mechanism of the formation of β-chlorovinylarsines proceeds through an intermediate additive compound of 1 molecule each of arsenous chloride and aluminum chloride and 3 moles of acetylene, $Al(CHCl.CHCl)_3As$. Subsequently, Lewis and Stiegler [193] pointed out various steps of the reaction which supports this assumption experimentally. Since in a fresh reaction mixture, the yield of primary and secondary chlorovinylarsines is increased by warming with free arsenous chloride, those compounds must be formed through the intermediates,



(I) (II) (III)

Compound I is probably formed when acetylene is conducted into arsenic trichloride containing aluminum chloride; and compounds II and III are formed by the further reaction of I with one or two more moles of arsenic chloride, respectively.

Ethylene acts somewhat like acetylene in reaction with arsenic trichloride. (β-Chloroethyl)dichloroarsine (b.p. 89-90°/12 mm) is prepared in very modest yield by passing a current of dry ethylene through a mixture of arsenic trichloride and aluminum chloride at 0°.[194]

Acetylene has been reacted with methyldichloroarsine, CH_3AsCl_2, in the presence of 40 per cent by weight of aluminum chloride at 10-15°. The product consisted of a mixture of (β-chlorovinyl)methylchloroarsine and bis-(β-chlorovinyl)methylarsine. They were isolated by treating the reaction mixture with 20 per cent hydrochloric acid, extracting with ether, and fractionating the extract at reduced pressure.[195]

Phosphorus.—Acetone condenses with phosphorus trichloride in the presence of aluminum chloride to yield diacetonylphosphorus chloride. Reaction is effected by gradual addition of 80 g of sublimed aluminum chloride to a mixture consisting of 500 g of phosphorus trichloride and 2.5 times the volume of methanol-free acetone, and heating gently until evolution of hydrogen chloride has ceased. The pure product (m.p. 35-36° and b.p. 154°/100 mm) is secured in a 10 per cent yield, based on the phosphorus trichloride employed.[196]

It has been claimed that aliphatic or cycloaliphatic hydrocarbons react with phosphorus trichloride in the presence of aluminum chloride to yield phosphorus derivatives. The reaction is believed to proceed by formation of a complex, $R.PCl_2.AlCl_3$, with evolution of hydrogen chloride. Addition of an alcohol to the complex yields an intermediate product which is converted to phosphinic acid ester upon hydrolysis [197]:

[193] W. L. Lewis and H. W. Stiegler, *J. Am. Chem. Soc.*, 47, 2546-2556 (1925).
[194] W. W. Nekrassow and A. S. Nekrassow, *Ber.*, 61, 1816-1821 (1928).
[195] H. N. Das-Gupta, *J. Indian Chem. Soc.*, 13, 305-308 (1936); *C. A.*, 30, 7098.
[196] A. Michaelis, *Ber.*, 17, 1273-1276 (1884); 18, 896-910 (1885).
[197] U. S. P. 2,137,792 (1938) to W. W. Woodstock (to Victor Chemical Works).

$$RH + PCl_3 \xrightarrow[-HCl]{AlCl_3} R.PCl_2.AlCl_3$$

$$R.P\begin{matrix}Cl.AlCl_3\\OR'\end{matrix} \xrightarrow[-HCl]{H_2O} R.P\begin{matrix}H\\OR'\end{matrix}=O + AlCl_3$$

Esters of phosphoric acid are obtained by treating phosphoryl chloride with olefin oxides in the presence of 0.5-5 per cent by weight (calculated on the oxyhalide) of aluminum chloride. The oxide is added in liquid or vapor form to the phosphoryl chloride containing the catalyst at such a rate that a substantial rise in temperature is avoided, the reactants being cooled or heated as required. Halogenated alkyl phosphates are produced, ethylene oxide yielding tris-(β-chloroethyl)phosphate [198]:

$$3(CH_2)_2O + POCl_3 \xrightarrow{AlCl_3} (CH_2Cl.CH_2)_3PO_4$$

Aluminum chloride may also be used as catalyst in the production of phosphoric acid esters from organic hydroxy- compounds and phosphoryl chloride or phosphorus pentoxide.[199]

Nitrogen.—Aluminum chloride forms a complex with ammonia which serves as an excellent dehydrating agent in the production of keto-imines from liquid ammonia and aliphatic or aralkyl ketones. Ammonolysis may also be effected by heating the ketone with ammonia in the presence of aluminum chloride. Thus, fenchoneimine is prepared by heating fenchone at 180° for four hours with 4 times its volume of anhydrous ammonia and an excess of aluminum chloride.[200]

The condensation of urea and acetic anhydride with production of varying proportions of acetylurea and cyanuric chloride has been shown to be catalyzed by aluminum chloride.[201]

Carbamyl chloride yields carboxylic acid amides by reaction with aliphatic or cycloaliphatic hydrocarbons in the presence of aluminum chloride. A stable molecular compound of carbamyl chloride and aluminum chloride may be used, and reaction is preferably conducted by heating at 100-200° in an autoclave.[202]

In an attempt to condense amides with benzene in the presence of aluminum chloride it was found that dehydration of the amide to nitrile occurred instead. This thus affords a convenient method for preparing nitriles. When molecular equivalents of acetamide and aluminum chloride were heated under reflux a 60 per cent yield of acetonitrile was obtained.[203]

[198] British P. 475,823 (1936) to A. J. Daly and W. G. Lowe (to Brit. Celanese); *Brit. Chem. Ab.*-B, 137 (1938).
[199] British P. 455,014 (1936) to Celluloid Corp.; *C. A.*, 31, 1427.
[200] H. H. Strain, *J. Am. Chem. Soc.*, 52, 820-823 (1930).
[201] J. Böeseken and M. J. Langeaal, *Rec. trav. chim.*, 29, 330-339 (1910); *C. A.*, 5, 678.
[202] U. S. P. 2,168,161 (1939) to H. Hopff, H. Kellermann, and A. Freytag (to I. G. Farbenindustrie).
[203] J. F. Norris and B. M. Sturgis, *J. Am. Chem. Soc.*, 61, 1413-1417 (1939).

Sulfur.—Thio-aliphatic acids may be prepared by reaction of acid chlorides with hydrogen sulfide in the presence of a small amount of aluminum chloride at low temperatures. Treatment of 50 g of chloroacetyl chloride containing 1 g of aluminum chloride with hydrogen sulfide for eight to nine hours with ice-cooling gives 24 g of chlorothioacetic acid. Analogously, a 40 per cent yield of thioacetic acid is secured from acetyl chloride.[204]

Hydrogen sulfide adds to ethylene oxide by heating molecular equivalents of the two reactants in a closed tube for 10 days at 8-10° to give a quantitative yield of thioethylene glycol.

$$C_2H_4O + H_2S \qquad HS\ CH_2.CH_2.OH$$

In the presence of certain catalysts, like mineral acids, aluminum chloride, or chlorides of heavy metals, the above reaction is accelerated.[205]

Metathetical Reactions with Metal Compounds

It has been claimed that when alkali or alkaline-earth alloys with lead or other elements of the fourth periodic group are reacted with an alkyl chloride or bromide under pressure and at a temperature above the boiling point of the alkyl halide and in the presence of a catalyst like metallic zinc or aluminum chloride, reaction takes place with formation of a metal alkyl. Reaction of the sodium alloy of lead with ethyl chloride occurs with formation of an ethyl compound of lead.[206]

Cleavage reactions have been shown to take place with phenyl- and ethyllead compounds in the presence of aluminum chloride[207]:

$$R_4Pb + AlCl_3 \rightarrow R_3PbCl + RAlCl_2$$
$$R_4Pb + RAlCl_2 \rightarrow R_4PbCl + R_2AlCl$$
$$R_3PbCl + AlCl_3 \rightarrow R_2PbCl_2 + RAlCl_2$$

With ethyllead compounds the R_2PbCl_2 compound was not isolated, aluminum chloride accelerated its decomposition to lead chloride, ethyl chloride and disproportionation products of the ethyl radicals.

In an extensive investigation of the effect of certain catalysts on metal alkyls,[208] it has been shown that random intermolecular exchange of organic radicals occurs. Mixtures of metal alkyls were heated in the presence of numerous catalysts, and it was found that reaction occurred with formation of all possible compounds. For example, tetramethyllead and triethyllead react to give a complex mixture of all five possible compounds containing either or both methyl and ethyl groups, as well as the four possible trialkyllead chlorides:

[204] F. Arndt and N. Bekir, *Ber.*, 63, 2390-2393 (1930)
[205] A. E. Chichibabin and M. A. Bestuzhev, *Compt. rend.*, 200, 242-244 (1935); *C. A.*, 29, 2509; *Brit. Chem. Abs.*-B, 606 (1935)
[206] British P. 214,221 (1923) to C. A. Kraus and C. C. Callis (to Standard Development Co.)
[207] H. Gilman and L. D. Apperson, *J. Org. Chem.*, 4, 162-168 (1939)
[208] G. Calingaert and H. A. Beatty, *J. Am. Chem. Soc.*, 61, 2748-2754 (1939). G. Calingaert, H. A. Beatty, and H. R. Neal, *ibid.*, 61, 2755-2758 (1939) G. Calingaert and H. Soroos, *ibid.*, 61, 2758-2760 (1939).

$$Me_4Pb + Et_4PbCl \longrightarrow Me_4Pb + Me_3EtPb + Me_2Et_2Pb + MeEt_3Pb + Et_4Pb + Me_3PbCl + Me_2EtPbCl + MeEt_2PbCl + Et_3PbCl$$

The reaction was found to be general for different R radicals, including methyl, ethyl, *n*-propyl, isopropyl, *s*-butyl, *t*-butyl, phenyl, and *p*-tolyl bound to one or more metals, including lead, tin, silicon, and mercury. No decomposition occurred; there was no evidence of evolution of gas, or precipitation of metal, or heat of reaction; recovery of reactants was complete except for possible loss through handling. Examples of metals which display interchange upon heating to the boiling point a mixture of a total of 0.3 mole of organometallic compound and 1 g of aluminum chloride in 50 ml of hexane and subsequent heating at 60-80° for five to seven hours are given:

$Me_4Pb + Et_4Pb$	$Et_4Si + Pr_4Si$ (at 180°)
$Me_4Sn + Et_4Sn$	$Me_4Sn + Et_4Pb$
$Me_2Hg + Et_2Hg$ (no solvent used)	$Et_2Hg + Me_4Pb$

Accurate material balance of redistribution effected in a mixture of tetramethyl- and tetraethyllead in hexane solution shows it to be quantitative, except for the fact that the aluminum chloride reacts irreversibly with the alkyl lead compounds [207] forming alkyl lead chlorides in very small quantities.

In redistribution reactions involving alkyl compounds of lead with those of mercury, mercury shows a greater relative affinity than lead for methyl with respect to ethyl radicals.[208a]

Isomerization of Paraffins and Cycloparaffins

When paraffinic hydrocarbons are treated with aluminum chloride under mild conditions, isomerization may occur with conversion to branched paraffins. The reaction is reversible, an equilibrium existing between the straight-chain paraffins and the branched constituents. It is accompanied by cracking, dehydrogenation, and polymerization of the resulting olefins. The following cases of isomerization with aluminum chloride which have been observed do not include the production of branched cleavage fragments:

Initial Paraffin	Conditions	% of the Branched Constituent in the Equilibrium Mixture	Ref.
n-Butane	150°/30 atm.; 20% $AlCl_3$+5% HCl	66.5% of isobutane	1, 11
n-Butane	70-110°	67-74% of isobutane	12
n-Butane	activated carbon impregnated with $AlCl_3$	isobutane	3
n-Butane	below 110°; HCl present	isobutane	13
n-Pentane	at 150°/pressure	27% of 2-methylbutane	1
n-Pentane	$AlCl_3$+HX; H_2O, or alkyl chlorides	liquid phase: chief product, 55.9% of 2-methylbutane; vapor phase: chief product, methylpropane	4
n-Pentane	>10% $AlCl_3$+>2% HCl at >200°/>10 atm.; granular carrier optional	2-methylbutane	2

[208a] G. Calingaert, H. Soroos, and G. W. Thomson, *J. Am. Chem. Soc.*, 62, 1542-1545 (1940).

Initial Paraffin	Conditions	% of the Branched Constituent in the Equilibrium Mixture	Ref
n-Pentane	$AlCl_3$ complex with aralkyl hydrocarbon used as catalyst	18.3% of isopentane	15
n-Hexane	at 68°	50% of 2-methylpentane	5
n-Hexane	3-8% $AlCl_3$ at below 100° for several hrs. or at room temp. with $AlCl_3$+HCl or alkyl halides	isomers of hexane	6
n-Heptane		4% of 2-methylhexane (of the n-heptane consumed)	7
n-Heptane		isoheptane dimethylpentane	5
n-Heptane		1.5% 2,4-dimethylpentane 1.6% 3-methylhexane 1.2% 2-methylhexane (above values based on the n-heptane consumed)	8
n-Heptane	1% $AlCl_3$ at 22° for 3 hrs./5 atm. H_2	8% of iso-compounds of heptane	10
n-Heptane	10% $AlCl_3$+HCl; 5 hrs. at 40°.	16% iso-compounds of heptane	14
n-Octane	10% $AlCl_3$+HCl; 1-2 hrs. at 50-60°.	31-37% of iso-octane	14
n-Octane	HCl had to be present with $AlCl_3$ to effect isomerization at room temperature	iso-compounds of octane	6
n-Octane	5% $AlCl_3$ at 405-410° for 3 hrs./70 atm. H_2	18% of iso-compounds of octane	
n-Octane	10% $AlCl_3$+HCl/room temp. and atm. pressure for 140 hrs	40% of iso-compounds of octane	

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9. A. P. Meshcheryakoo and E. P. Kaplan, *Bull. acad. Sci. (U.S.S.R.) Classe sci. math. nat. Sci. chim.*, 1055-1060 (1936); *C. A.*, 33, 6230.
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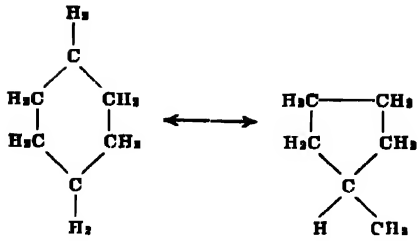
12. B. L. Moldavskii and T. V. Nizovkina, *J. Gen. Chem. (U.S.S.R.)*, 9, 1652-60 (1939); *C. A.* 34, 3069. *Natl. Petroleum News*, Nov. 27, 1940.
13. Brit. P. 509,540 (1939) to N. V. de Bataafsche Petr. Maatschappij; *C. A.*, 34, 3766. cf Brit. P. 516,650 (1940), *J. Inst. Petroleum*, 26, 150A (1940); and French P. 841,979, *C. A.*, 34, 4395, both to N. V. de. Bataafsche Petr. Maatschappij.
14. A. P. Sivertsev, *J. Gen. Chem. (U.S.S.R.)*, 10, 799-802 (1940); *Natl. Petroleum News*, March 5, 1941.
15. Dutch P. 48,338 (1940) to W. C. B. Smithuysen (to N. V. de Bataafsche Petr. Maatschappij) *C. A.*, 34, 7934.

Cyclohexane isomerizes to methylcyclopentane in the presence of aluminum chloride.[209] It has been found by Nenitzescu and Cantuniari[210] that freshly sublimed, anhydrous aluminum chloride scarcely affects cyclohexane. With aluminum chloride containing water, a reversible isomerization occurs:

[209] O. Aschan, *Ann.*, 324, 1-39 (1902). N. D. Zelinskii and M. B. Turova-Pollak, *Ber.*, 65, 1171-1174 (1932), *C. A.*, 26, 5080. N. D. Zelinskii and M. B. Turova-Polyak, *J. Gen. Chem. (U. S. S. R.)*, 2, 666-670 (1932), *C. A.*, 27, 2429.

[210] C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, 66, 1097-1100 (1933). *Brit. Chem. Abs.*-A, 941 (1933)



At the boiling point, the equilibrium mixture was found to consist of about 78 per cent of cyclohexane and 22 per cent of methylcyclopentane. The transformation of cyclopentane into methylcyclopentane does not seem to be due to the smaller strain of the cyclopentane ring, for the strain-free cyclohexane ring appears more stable and less reactive.

Since the isomerization of cyclohexane is reversible, aluminum chloride acts on methylcyclopentane to yield cyclohexane. An equilibrium mixture containing 84 per cent cyclohexane and 16 per cent methylcyclopentane has been reported. Ethylcyclopentane gives an equilibrium mixture containing 97 per cent of methylcyclohexane.[211] Propylcyclopentane likewise is converted to a six-membered ring.[212] Isomerization of the higher alkyl cyclopentanes is accompanied by cleavage of the alkyl group, as shown in the following conversion [213]:

ethylcyclopentane: methylcyclohexane
propyl- or isopropylcyclopentane: 1,3-dimethylcyclohexane
n, *s*, or *t*-butylcyclopentane: 1,3,5-trimethylcyclohexane

The isomerization was effected at 50°; over 80 per cent yields of isomerized products were obtained.[214]

Glasebrook and Lovell [215] have shown that the reaction of cyclohexane or methylcyclopentane in the presence of aluminum chloride promoted by water or hydrogen chloride results in an equilibrium consisting principally of the two hydrocarbons. With cyclohexane, not more than 5 per cent of the hydrocarbon is used in side reactions. These investigators determined the equilibrium constants for the isomerization reaction at 10° intervals, from 25 to 77.4°. These data were used to compute values of the free energy change, heat of reaction, and entropy change. These same constants calculated from specific heat data are in poor agreement with those obtained from the equilibrium measurements.

When cyclohexane was treated with aluminum chloride and hydrogen chloride in the absence of air in a closed autoclave for 24 hours at 150°,

[211] M. B. Turova-Pollak and N. B. Baranovskaya, *J. Gen. Chem. (U. S. R. R.)*, 9, 429-431 (1939); *C. A.*, 33, 9293. M. B. Turova-Pollak and Z. Makaeva, *J. Gen. Chem. (U. S. S. R.)*, 9, 1279-82 (1939); *C. A.*, 34, 727.

[212] M. B. Turova-Pollak and O. I. Polyakova, *J. Gen. Chem. (U. S. S. R.)*, 9, 233-238 (1939); *C. A.*, 33, 6254.

[213] H. Pines and V. N. Ipatieff, *J. Am. Chem. Soc.*, 61, 1076-1077 (1939); *ibid.* Paper presented to American Chemical Society, Baltimore, 1939.

[214] For isomerization of butylcyclopentane see M. B. Turova-Pollak and A. F. Koshelev, *J. Gen. Chem. (U. S. S. R.)*, 9, 2179-83 (1939); *C. A.*, 34, 4058.

[215] A. L. Glasebrook and W. G. Lovell, *J. Am. Chem. Soc.*, 61, 1717-1720 (1939); *ibid.*, Paper presented to the Organic Division, American Chemical Soc., Baltimore, 1939.

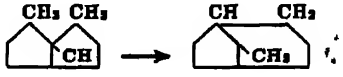
not only isomerization to methylcyclopentane, but also dehydrogenation was found to occur. A subsequent combination of two cyclohexyl radicals to form a mixture of dimethylbicyclopentyl and bicyclohexyl took place.[216]

Grignard and Stratford [217] have reported that cyclohexane and methylcyclohexane are not changed at 120-150° in the presence of 20-30 per cent by weight of aluminum chloride. Like treatment of *o*- and *p*-dimethylcyclohexanes, however, revealed an isomerism into the *m*-derivative, the *p*-compound undergoing the change more easily. Cyclohexane with C_2 and C_3 side-chains was cracked only to the extent of 1 to 5 per cent. The remainder was isomerized to *m*-methyl derivatives; *m*-diethylcyclohexane was found to yield largely tetramethylcyclohexane. The three butylcyclohexanes gave a mixture of tetramethylcyclohexanes as the principal product. Amyl and isoamyl cyclohexanes gave more cleavage products, but methylcyclohexane was also formed, together with tetra- and pentamethylcyclohexanes.

Alkyl derivatives of cyclohexane have been shown to isomerize when heated with 10 per cent of finely ground aluminum chloride at 120-130°. Methyl-, dimethyl-, and ethylcyclohexanes are converted to five-membered rings.[218] Boiling methylcyclohexane is changed to the extent of 1 per cent to 1,2-dimethylcyclopentane.[219] The reaction is reversible.

It has been shown by Zelinsky and Turova-Pollak [220] that aluminum chloride acts on *cis*-decalin to convert it irreversibly into the trans-isomeride: the *cis*- form of the decalin is first isomerized under the influence of aluminum chloride and is then transformed into a bicyclic system composed of 2-pentamethylene rings. Cleavage products are formed simultaneously.[221] According to Jones and Linstead,[222] isomerization of decalin proceeds with formation of dimethyl-0,3,3-bicyclooctane. The material from decalin probably has the *trans*- configuration.

When *cis*-0,3,3-bicyclooctane is allowed to stand at room temperature in contact with aluminum chloride, it is converted into a crystalline isomeride, m.p. 132°, which is probably 1,2,3-bicyclooctane [223]:



The isomerizing effect of aluminum chloride is apparent in the 30-44 per cent conversion of pinene to camphene upon heating with a mixture

[216] V. N. Ipatieff and V. I. Komarewsky, *J. Am. Chem. Soc.*, **56**, 1926-1928 (1934).
[217] V. Grignard and R. Stratford, *Compt. rend.*, **178**, 2149-2152 (1924); *C. A.*, **18**, 3110.
[218] M. B. Turova-Pollak and N. D. Zelinskii, *Ber.*, **68**, 1751-1755 (1935); *C. A.*, **29**, 7951
[219] C. D. Nenitzescu, E. Ciorănescu, and I. P. Cantuniari, *Ber.*, **70**, 277-283 (1937); *cf. Angew Chem.*, **52**, 231-235 (1939).
[220] N. Zelinsky and M. B. Turova-Pollak, *Ber.*, **58**, 1299-1301 (1925); **58**, 1292 (1925); **62**, 1658-1663 (1929).
[221] N. D. Zelinskii and M. B. Turova-Polyak, *J. Applied Chem. (U. S. S. R.)*, **7**, 753-756 (1934), *C. A.*, **29**, 2328.
[222] R. L. Jones and R. P. Linstead, *J. Chem. Soc.*, 616-621 (1936).
[223] J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611-616 (1936).

of aluminum chloride and magnesium chloride, or a 30-56 per cent conversion by heating with aluminum chloride and aluminum oxide.[224]

Dicyclohexyl, heated with aluminum chloride at 100° for 50 hours, yields chiefly *trans*-bicyclohexyl (b.p. 217-219°), from which 2,6-dimethylnaphthalene is obtained by dehydrogenation.[225]

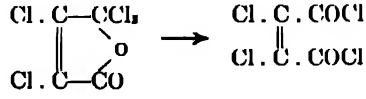
Isomerization occurs during cracking of hydrindane with aluminum chloride.[226] When hydrindane is heated at 170-230° for ten hours with the catalyst, it forms 23 per cent of hexamethylene hydrocarbons, 66.5 per cent of pentamethylene hydrocarbons, and 10.5 per cent of saturated aliphatic hydrocarbons. The 5-membered ring of hydrindane is very stable toward isomerization, but the 6-membered ring splits easily and tends to isomerize to a 5-membered ring, giving bicyclic hydrocarbons with two 5-membered rings.

Isomerization accompanying Friedel-Crafts reactions is discussed under Friedel-Crafts alkylation.*

Miscellaneous Isomerizations

Chlorofumaric acid chloride is isomerized to the extent of 85-87 per cent into chloromaleic acid chloride when heated on a water-bath with a molar equivalent of aluminum chloride.[227] Dibromofumaric acid chloride is likewise isomerized, but during the reaction an exchange of halogen also occurs, so that the product is dichloromaleic acid chloride.

The unsymmetrical form of dichloromaleic acid chloride is converted into the symmetrical form by aluminum chloride[228]:



The sensitivity of dicarboxylic acid chlorides to aluminum chloride depends upon the comparative stability of the isomeric forms. The fact that succinyl chloride is not isomerized by treating it with aluminum chloride, under the same conditions which result in conversion of fumaryl chloride to maleic chloride, is probably due to the fact that the symmetric and unsymmetric forms of succinyl chloride are in equilibrium with each other.[227]

Aluminum chloride catalyzes a stereochemical rearrangement of sugars.[229]

[224] S. Komatsu and C. Fujio, *Mem. Coll. Sci. Kyoto Imp. Univ. Series*, 7A, No. 6, 389-395 (1924); *C. A.*, 19, 2818.
[225] R. J. Levina, J. K. Juriev, and A. I. Loschkomoinikov, *J. Gen. Chem. (U. S. S. R.)*, 7, 341-349 (1937); *Brit. Chem. Abs.*-A (II), 336 (1937).
[226] M. B. Turova-Pollak and F. I. Podol'skaya, *J. Gen. Chem. (U. S. S. R.)*, 7, 1738-1741 (1937); *C. A.*, 32, 558.
* See page 94.
[227] E. Ott, *Organic Syntheses*, 11, 88-91 (1931); *Ann.*, 392, 245-285 (1912).
[228] L. Leder, *J. prakt. Chem. (2)*, 130, 255-288 (1931); *C. A.*, 25, 4224; *C. Z.*, 1931 II, 537.
[229] A. Kunz and C. S. Hudson, *J. Am. Chem. Soc.*, 48, 2435 (1926). C. S. Hudson and J. M. Johnson, *J. Am. Chem. Soc.*, 38, 1223-1228 (1916). L. Kahlenberg, D. J. Davis, and R. E. Fowler, *J. Am. Chem. Soc.*, 21, 1-23 (1899), *J. Chem. Soc. Abs.*, 76 (II), 470 (1899).

Cyclizing Activity of Aluminum Chloride

In 1902, Aschan [230] suggested that the presence of naphthenes in mineral oils may be due to cyclization of compounds of the olefin series which result from the initial decomposition of fossil fat. Laboratory experiments, using aluminum chloride for cyclization of pentene to methylcyclobutane substantiated his theory.[231]

According to Engler,[232] however, naphthenes are not formed from amylene and aluminum chloride at the ordinary temperature, nor by boiling methylcyclobutane. He suggested that naphthenes in natural petroleum are produced partly by direct condensation of olefins. An intermediate polymerization to viscid oils of high molecular weight and subsequent decomposition of these products to naphthenes is postulated. Experiments [233] with commercial pentene (b.p. 37-38°) and aluminum chloride showed production of little, if any, naphthenes. Heating amylene with aluminum chloride under various conditions led to formation of gases, but other products, boiling up to about 200° and consisting essentially of hydrocarbons of the series C_nH_{2n+2}, were also obtained.

Other investigators, however, substantiate the cyclizing activity of aluminum chloride. The cyclization of pentene into cyclopentane has been noted by Cox.[234] According to Nenitzescu and Dragan,[235] the action of aluminum chloride on hexane and heptane results not only in isomerization, dehydrogenating condensation to higher hydrocarbons and cleavage of the chain to lower paraffins, but also to a dehydrogenating cyclization to mono- and bicyclic paraffins. Hexane yields cyclohexane and 2- or 3-methylpentane. With heptane, accompanying side reactions result in the formation of 1,3-dimethylcyclohexane, methylcyclohexane, cyclohexane, and bicyclic paraffins, together with isomerization and cleavage products.

The conversion of butenes to a mixture of naphthenes by aluminum chloride has been patented.[236] When liquefied butene is treated with aluminum chloride in the proportion of 28 g of the former to 0.5 g of the latter, and the temperature is kept below −10°, after two hours there is obtained a practically quantitative yield of naphthenes distilling as follows:

260-290°/17 mm	8 g
270-350°/17 mm	13 g
above 350°/17 mm	5 g

The presence of aromatic hydrocarbons in distillates obtained by cracking petroleum with aluminum chloride is tied up with the cyclizing, cracking, and hydrogenating activity of the catalyst. It is possible that naphthenes, formed by cyclization of olefins are dehydrogenated to aro-

[230] O. Aschan, *Ann.*, 324, 1-89 (1902); *J. Chem. Soc. Abs.*, 82 (I), 749 (1902).
[231] O. Aschan, "Naphthenverbindungen, Terpene und Campherarten," W. de Gruyter & Co., Berlin and Leipzig, 1920, p. 8-10. O. Aschan, *Oversikt Finska. Vet. Soc.*, 58, 43 (1916).
[232] C. Engler, *Ber.*, 42, 4810-4813 (1909).
[233] C. Engler and O. Routala, *Ber.*, 42, 4813-4820 (1909).
[234] M. V. Cox, *Bull. soc. chim.*, 37, 1549-1553 (1925); *C. A.*, 20, 899.
[235] C. D. Nenitzescu and A. Dragan, *Ber.*, 66, 1892-1900 (1933); *C. A.*, 28, 1025.
[236] British P. 168,482 to C. Weizmann and D. A. Legg, *J. Chem. Soc. Abs.*, 120, 712 (1921).

matic hydrocarbons.[237] Pictet and Lerczynska[238] suggest formation of alkylated saturated naphthene nuclei, which are cracked by aluminum chloride in such a manner that the side chains entrain with them hydrogen atoms from the nuclei, with a consequence that the nuclei become unsaturated aromatic hydrocarbons.

Occurrence of aromatic hydrocarbons in gasolines obtained by cracking in the presence of aluminum chloride has been frequently mentioned.[239] The kerosene fraction obtained by cracking Perm crude oil has been reported to contain 60 per cent of aromatic hydrocarbons, and the gas oil 65 per cent of aromatic hydrocarbons.[240] Cracking paraffin oils with aluminum chloride has been noted to give an oil containing 24 per cent of aromatic hydrocarbons.[241]

Increased yields of aromatic hydrocarbons are obtained if cracking of kerosene is conducted in the presence of nascent aluminum chloride such as is produced by using aluminum and hydrogen chloride as cleavage agents, or in the presence of aluminum chloride and hydrogen.[242] The effect of nascent aluminum chloride on a hard paraffin consisting of pentacosane has been contrasted with that of anhydrous aluminum chloride under the same conditions.[243] With nascent aluminum chloride at 210-220° for 40 hours, about 80 per cent of gasoline was secured. This was distilled into 5-degree fractions from 30 to 122°, in which were found from 4.08 to 46.0 weight percent of aromatic hydrocarbons. Using anhydrous aluminum chloride, the weight percentage of aromatic hydrocarbons was only 2.25 to 6.10.

In an investigation of the use of various chlorides in the catalytic cracking of gasoline, it has been found that nascent aluminum chloride is especially active in raising the aromatic and paraffin contents of the product at the expense of the olefins and naphthenes. The distillate below 150° was increased ten- to twentyfold.[244]

The greater cyclizing reactivity of nascent aluminum chloride over anhydrous aluminum chloride has been attributed to the reducing power of the nascent hydrogen, released in the formation of aluminum chloride, which retards the polymerization of the unsaturated bodies.[245]

[237] *Cf.* N. D. Zelinskiĭ and M. E. Mikhlin, *J. Applied Chemistry (U. S. S. R.)*, 6, 16-19 (1933); *C. A.*, 27, 5176.

[238] Ame Pictet and I Lerczynska, *Arch. sci phys nat.*, 44, 400-401 (1917); *C. A.*, 13, 182

[239] Dubrov, Lavrovskii, Goldstein, Fish, and Mikhnovskaya, *Neftyanoe Khozyaistvo*, 22, 19-25 (1932); *C. A.*, 26, 2353. N. D. Zelinskiĭ and M. E. Mikhlin, *J. Applied Chemistry (U. S. S. R.)*, 6, 16-19 (1933); *C. A.*, 27, 5176. C Otin and S Savencu, *Petroleum Z.*, 34, No. 46, 1-5, No. 47, 1-5 (1938); *C. A.*, 33, 8966 S. S Nifontova and M G Pogorelova, *Bull. Far East Branch Acad. Sci U. S. S. R.*, No. 24, 3-9 (1937); *C. A.*, 31, 8899 B T Brooks and I W. Humphrey, *J. Am. Chem. Soc.*, 38, 398-400 (1916); *C. A.*, 10, 683. A. P. Lidov, *Petroleum*, 12, 413-427 (1917); *C. A.*, 13, 3005.

[240] Yu. K. Yur'ev, *Neftyanoe Khoz.*, No. 2 56-59 (1936); *C. A.*, 31, 2795

[241] J. Tichy, *Paliva a Topeni*, 11, 85-89, 100-102 (1929); *C. A.*, 24, 4925

[242] C. Otin and M. Dima, *Petroleum Z.*, 33, No 12, 1-7 (1937); *C. A.*, 31, 8167.

[243] C. Otin and M. Dima, *Chim. et Ind.*, 40, 217-227 (1938); *Brit Chem Abs.*-B, 1256 (1938)

[244] C Otin and S. Savencu, *Petroleum*, 34, No. 46, 1-5; No. 47, 1-5 (1938), *Brit. Chem Abs.*-B, 10 (1939).

[245] C. Otin and M. Dima, *Monit. Petr. roum.*, 39, 1613-1620 (1938); *J. Inst Petroleum*, 25, 17A

Chapter 18

Polymerization

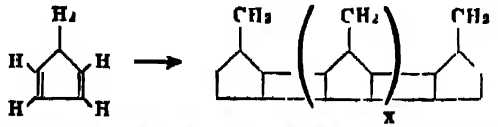
Anhydrous aluminum chloride is a powerful polymerizing agent as well as a condensation agent. It may be considered a two-edged sword aluminum chloride will polymerize various unsaturated hydrocarbons, but if these same polymerized hydrocarbons are left in the presence of anhydrous aluminum chloride, or subjected to more drastic conditions, they will decompose, or crack, or dealkylate into smaller units. Therefore, anhydrous aluminum chloride is an erratic polymerizing agent at best, and must be handled with care if high molecular weight compounds are to be obtained. It may be well for the sake of clarity and for the sake of nomenclature to review hastily some of the work which has been done in the field of high molecular weight compounds.

Staudinger[1] discriminates between three main groups of molecular colloids of macromolecules.

(1) Hemicolloids with a molecular weight up to 10,000 corresponding to an order of polymerization equal to 20 to 100 units
(2) Mesocolloids of the order of polymerization of 100 to 1000 having a chain length of 250 to 2500 Å units
(3) Eucolloids, substances of extremely high molecular weight, with polymerization units of over 1000 and chain lengths of over 2500 Å units.

These long-chain molecules have the characteristic properties of lyophilic colloids Their solution is accompanied by intense swelling of the solvent in which they are placed, and if soluble at all the dilute solutions are highly viscous. They show a high capacity for film formation and are often highly elastic. Whereas some unsaturated compounds, such as a styrene, acrylic esters, vinyl esters, etc , can give hemi-, meso-, or eucolloid products, according to the method in which they are polymerized, other compounds yield hemicolloids only.

These long-chain polymers result from the condensation or addition of compounds having two functional groups. If one or both of the reactants contain more than two functional groups, two-dimensional or three-dimensional polymers are formed. In the polymerization of cyclopentadiene, a completely insoluble two-dimensional product was obtained.[2]

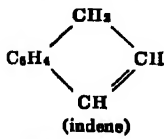
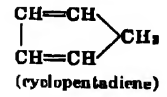


[1] H. Staudinger, "Die hochmolekularen organischen verdindungen Berlin," J Springer,
[2] H. Staudinger and H. A Bruson, *Ann*, 447, 97-110 (1926)

Three-dimensional structures have been assigned to phenolic and alkyd resins.[8] The cross linkages in this type of polymer result in an insoluble or infusible resin. Heat-convertible resins belong to this type.

Usually hydrocarbons like indene and styrene give polymers of relatively short-chain molecules. The following table gives a list of unsaturated hydrocarbons and the various types of colloids which can be produced from them.

Some Polymerisation Properties of Unsaturated Hydrocarbons Obtainable from Cracked Distillates **

Basic Molecule	Conditions of Polymerization	Solubility of the Polymer	Kind of the Polymeric Products	Order of Polymerization	Ref.
$CH_2=C(CH_3)_2$ (isobutene)	catalytic	easily soluble in C_6H_6, CCl_4, etc.; insoluble in acetone	from hemi-colloid to eucolloid	10-1000	*Helv. Chim. Acta*, 13, 1375 (1930).
$CH_2=CH.C_6H_5$ (styrene)	spontaneous and catalytic	easily soluble in C_6H_6, CCl_4, etc.; insoluble in acetone	eucolloid to hemicolloid	10-5000	*Ber.*, 62, 241, 2912, 2921.
$CH_2=CH.CH=CH_2$ (butadiene-1,3)	thermal and catalytic	easily soluble in C_6H_6, CCl_4*	from hemi-colloid to eucolloid	10-1000	*Ber.*, 67, 1171 (1934).
 (indene)	catalytic	soluble in C_6H_6, CCl_4	hemi-colloid	10-100	*Helv. Chim. Acta*, 12, 934 (1929).
 (cyclopentadiene)	spontaneous and catalytic	soluble in organic solvents	dimolecular hemi-colloid	2 to approx. 100	*Ann.*, 447, 97, 110 (1926).

* Often only limited swelling polymers are formed; see H. Staudinger and W. Heuer, *Ber.*, 67, 1171 (1934).

** H. Staudinger, *Trans. Faraday Soc.*, 32, 102 (1936).

It will be seen that all of these studies have been made on the polymerization of single compounds. The number of synthetic substances can be further increased by polymerization of a combination of compounds, or in other words, by polymerization mixtures of different unsaturated substances. Polymerized products of these combinations of compounds are of great technical interest. The complicated structure of the resulting polymers makes it exceedingly difficult for the investigator to follow their path of polymerization. Since it it well known that the hemicolloids are in general the most soluble, they lend themselves to applications where solubility is desired, such as in the surface-coating industry.

Various workers in the field of polymerization have established that when polymerization takes place with formation of a long chain, the resulting polymer is soluble. When polymerization takes place in three dimensions, the resulting polymer is insoluble and is usually "infusible." As has been mentioned, styrene is an example of long-chain polymer; examples of three-dimensional or space polymers are phenol formalde-

[8] W. H. Carothers, *Chem. Rev.*, 8, 403-404 (1931).

hyde condensation products. Products of straight-chain polymerization, for example styrene, are generally much more soluble than a polymer of phenol and formaldehyde with the same molecular weight. However, in polymerizing to form macro-molecules of great length, styrene uses up its only available bond and the resulting polymer theoretically has practically zero iodine value.[4] This may be one of the reasons why styrene undergoes so few side reactions to form three-dimensional polymers, but continues to form a straight chain. Therefore, the macro-molecule of styrene is generally unreactive chemically. Data have been offered to support the assumption that polystyrenes contain one double bond per molecule (the terminal double bond) no matter what the size of the molecule.[5]

Diolefins, on the other hand, with the proper catalyst, also polymerize to straight chains, but because of the manner of addition, it is possible to obtain a straight-chain polymer of isoprene which has a rather high molecular weight but still has a high iodine value.

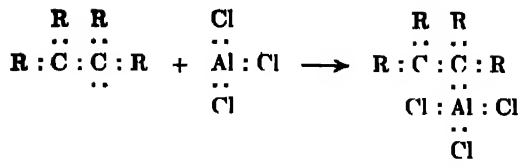
Aluminum chloride usually is employed as a catalyst only with hydrocarbons; with compounds containing oxygen or elements other than carbon and hydrogen there is usually a reaction between the oxygen or other element and the aluminum chloride, forming a complex which modifies the effect of the aluminum chloride.

The use of aluminum chloride, as well as other halides, as a polymerizing catalyst has been comprehensively reviewed in several texts dealing especially with polymerization.[6]

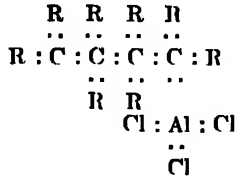
Polymerization of Olefins with Aluminum Chloride

Olefins in general have a great affinity for aluminum chloride. For example, when a solution of an olefin in an inert solvent like carbon disulfide is agitated with aluminum chloride, the entire olefin is precipitated on the aluminum chloride and the resulting carbon disulfide layer is olefin-free. The reaction is nearly quantitative. This same phenomenon occurs with other olefins such as propylene, butylene, amylene, and other higher molecular weight olefinic compounds. Usually the polymers are not of great molecular weight, that is, the products are generally hemicolloids and are of an oily or semi-solid nature. This phenomenon has been made use of in the manufacture of lubricating oils, where aluminum chloride is agitated with various olefins to form a high-grade lubricant or motor fuel. In the polymerization of olefins with aluminum chloride a theory of polymerization based on the electronic structures of aluminum chloride and olefins has been advanced.[7] Here we have first a coupling of the olefin with the metal halide which can be represented as follows:

[4] W. H. Carothers, *Chem. Rev.*, **8**, 395 (1931).
[5] G. S. Whitby, *Trans. Faraday Soc.*, **32**, 215-223 (1935).
[6] Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp. 1935. R. E. Burk, H. E. Thompson, A. J. Weith, and I. Williams, "Polymerization," New York, Reinhold Publishing Corp., 1937.
[7] W. W. Hunter and R. V. Yohe, *J. Am. Chem. Soc.*, **55**, 1248-1252 (1933).



This complex is a highly activated molecule by virtue of the one carbon which is momentarily three covalent. If it should come into contact with another molecule of an olefin, immediate combination would result. This new complex,



would still be in an activated state, and could, therefore, react with another molecule of an olefin in the same manner. The chain grows very rapidly through the formation of complexes. The length of the chain will depend on the heat of reaction, the ability of the coördinate bond to maintain this combination, and the possibility of ring formation Assuming that the complex combines with additional molecules of olefins, and that the hydrocarbon chain grows in the complex itself, it is difficult to understand and explain the fact that olefins of various molecular weights are always found in the reaction products.

Isobutylene polymerizes readily in the presence of anhydrous aluminum chloride, and if the reaction is kept at extremely low temperatures, in a suitable solvent relatively high molecular weight polymers can be obtained. These, however, are still in the hemicolloid class.[8] Boron trifluoride will polymerize isobutylene at a temperature of −80° or below, to form high molecular weight polymers ranging from hemicolloids to eucolloids, where the order of polymerization is from 10 to over 1000 units.[9] Since there is only one double bond available in these simple olefins, the resulting polymers, particularly if they are of high molecular weight, are practically saturated and are relatively stable to chemical reactivity.

In the polymerization of olefins with aluminum chloride, the addition of hydrogen chloride increases the reaction velocity and generally changes the character of the reaction. Pure ethylene has been found not to polymerize in the presence of really pure aluminum chloride even under pressures up to 50 atmospheres at 10-50°; the presence of traces of hydrogen chloride or moisture is necessary for the reaction.[10] This would indicate that the mechanism of olefin polymerization consists of a preliminary

[8] W. H. Hunter and R. V. Yohe, *J. Am. Chem. Soc.*, 55, 1248-1252 (1933).
[9] *cf.* British P. 401,297 (1933) to I. G., *C. A.*, 28, 2367; British P. 432,106 (1935) to I. G., *C. A.*, 30, 109.

aluminum chloride-catalyzed addition of hydrogen chloride. The alkyl chloride thus formed unites with a molecule of olefin, thereby losing hydrogen chloride which is again used for the transformation of another molecule of an olefin into an alkyl chloride. In the case of ethylene, the reactions occurring could be portrayed thus:

$$CH_2 : CH_2 + HCl \xrightarrow{AlCl_3} CH_3CH_2Cl$$

$$CH_3CH_2Cl + CH_2 : CH_2 \xrightarrow{AlCl_3} CH_3CH_2CH_2 : CH_2 + HCl$$

$$CH_2 : CH_2 + HCl \xrightarrow{AlCl_3} CH_3CH_2Cl$$

$$CH_3CH_2Cl + CH_3CH_2CH_2 : CH_2 \xrightarrow{AlCl_3} CH_3CH_2CH_2CH_2CH_2 : CH_2 + HCl$$

High molecular polymers of ethylene are not formed because of hydrogen disproportionation of the mono-olefin into a mixture of paraffins and unsaturated naphthenes. In an investigation of the action of aluminum chloride on a number of aliphatic olefins (ethylene, butylene, pentenes, octenes, decenes, and hexadecene) at temperatures of -78 to $+70°$, the products obtained were liquid.[11] Cyclization was found to occur at polymerization temperatures as low as $-78°$. In this study the effect of a large quantity of hydrogen chloride on the action of aluminum chloride was also made apparent. Where aluminum chloride alone did not give rise to material polymerization, considerable quantities of high molecular products were formed on the addition of hydrogen chloride gas These researches thus stress the importance of hydrogen chloride in polymerization with aluminum chloride, and question the role played by activated aluminum chloride complexes hitherto discussed. That the part played by hydrogen halides is noteworthy is evident when it is realized that those olefins which add a molecule, HX, most readily, also polymerize most readily.[12]

Several well-substantiated theories dealing with the catalytic polymerization of olefins have been discussed, and it has been shown that generally there is assumed the formation of an intermediate compound resulting from the addition of hydrogen,[12] hydrogen chloride, phosphoric acid,[13] or metal halides to the olefin. The formation of such intermediate addition compounds, however, cannot explain the thermal polymerization of olefins. Although no extensive mention will be made here of the various explanations which have been advanced for the thermal polymerization of olefins, it should be pointed out that these are necessarily based on changes in which the olefin molecule itself is involved. There may be either a preliminary dehydrogenation[14] or a momentary formation of

[10] V. N. Ipatieff and A. V. Grosse, *J. Am. Chem. Soc.*, **58**, 913-917 (1936).
[11] H. I. Waterman and J. J. Leendertse, *J. Inst. Petr. Tech.*, **24**, 16-37 (1938).
[12] F. C. Whitman, *Ind. Eng. Chem.*, **26**, 94-95 (1934).
[13] V. N. Ipatieff and H. Pines, *Ind. Eng. Chem.*, **28**, 684-686 (1936).
[14] The formation of acetylene [*cf.* W. A. Bone and H. F. Coward, *J. Chem. Soc.*, **93**, 1197-1225 (1908)] and of dienes [*cf.* R. V. Wheeler and W. L. Wood, *J. Chem. Soc.*, 1919-193] has been postulated.

divalent [15] or free radicals.[16] Explanation of catalytic polymerization by the formation of addition compounds with the catalyst, therefore, must not be construed as an attempt to explain other processes of olefin polymerization.

Application of Polymerization Products from Olefins

Branched-chain olefins give viscous, semi-solid products having a molecular weight of 800-10,000 by treatment with aluminum chloride at temperatures below $-10°$.[17] Since isoölefins are more readily polymerized than straight-chain olefins, treatment of a mixture of olefins with aluminum chloride for a limited time (suitably about one minute) results in preferential polymerization of the branched constituents.[18]

The high molecular polymerization products obtained by treatment of olefins with aluminum chloride may be sulfated to yield detergents.[19]

Polymerization products secured by reaction of lower unsaturated hydrocarbons with aluminum chloride are most extensively used as motor fuels or lubricants. Literature on this application is given in Table 36.

Investigations dealing with the polymerization of pure olefins and cyclo-olefins are listed:

Table 35

Olefin	References*	Olefin	References*
Ethylene	2, 5-8, 13-15, 17-20, 25a, 26, 29, 31-33, 38, 44, 45	Isobutene (+pentane)	41
		Pentene	1, 6b, 9-11, 21, 25, 33, 36
Ethylene (+HBr)	12	Pentene (+petroleum ether)	45
Ethylene (+HCl)	4	Pentene (+C_2H_5OH)	16
Ethylene (+gasoline)	46	Pentene-(1)	24
Ethylene (+naphtha)	30	Pentene-(2)	24, 35, 36, 40, 42
Ethylene (+C_2H_5OH)	16	2-Methyl-butene-(1)	24
Ethylene (+petroleum ether)	45	2-Methyl-butene-(2)	24, 42
Propene	22, 31, 44	3-Methyl-butene-(1)	23, 24, 35
Propene (+nitrobenzene)	43	3-Methyl-butene-(1) (+benzene)	35
Propene (+naphtha)	30	2-Methyl-butene-(1) (+HCl)	24
Propene (+petroleum ether)	45	2-Methyl-butene-(2) (+naphtha)	30
Propene (+C_2H_5OH)	16	2-Methyl-butene-(1) (+naphtha)	30
Butene	44	Hexene-(1) (+naphtha)	30
Butene-2	46	Octene	25, 31
Butenes	33	Octenes	33
Butenes (+petroleum ether)	45	Octene-(1) (+naphtha)	30
Butene-1 (+naphtha)	30	Decenes	33
Butene-2 (+naphtha)	30	Hexadecene	32
Butene (+ethyl alcohol)	16	Cetene	30
Isobutene	17, 18, 21, 31, 34, 39, 42	Cyclohexene	25, 27a, 32, 33, 34, 37
Isobutene (+naphtha)	30	Pinene	22a, 34a, 6a, 29a
Isobutene (+nitrobenzene)	43	*asym*-Diphenylethylene	3
Isobutene (+nitromethane)	43		

[15] C. Hurd, *Ind. Eng. Chem.*, 26, 50-55 (1934).

[16] E. Berl and W. Forst, *Z. angew. Chem.*, 44, 193-197 (1931). G. M. Kline and N. L. Drake, *J. Res. Nat. Bur. Stds.*, 13, 705-712 (1934).

[17] British P. 401,297 (1932), *Brit. Chem. Abs.*-B, 136 (1934); British P. 421,118 (1934), *C. A.*, 29, 3353; French P. 44,501 (1935), *C. A.*, 29, 6244; U. S. P. 2,124,225 (1938) to M. Mueller-Cunradi, M. Otto, W. Daniel, and R. Werner; U. S. P. 2,097,468 to H. Rabe and M. Otto (all to I. G. Farbenindustrie; British P. 503,736 (1938), *Brit. Chem. Abs.*-B, 804 (1939); British P. 509,463 (1938); French P. 838,064 (1939), *C. A.* 33, 7440; U. S. P. 2,049,062 (1936) to F. A. Howard (last 4 patents assigned to Standard Oil Development Co.); U. S. P. 2,085,524 (1937) to M. de Simo and F. B. Hilmer (to Shell Development Co.).

[18] British P. 466,066 (1936) to Standard Oil Development Co., *Brit. Chem. Abs.*-B, 757 (1937); U. S. P. 2,065,474 (1936) to M. Mueller-Cunradi and M. Otto (to I. G. Farbenindustrie), *C. A.*, 31, 1040; U. S. P. 2,099,090 (1937) to W. L. Webb (to Standard Oil Co. of Indiana), *C. A.*, 32, 209; U. S. P. 2,126,001 (1938) to S. C. Fulton and T. Cross, Jr. (to Standard Oil Development Co.).

[19] Brit. P. 401,297 (1933) to I. G., *C. A.*, 28, 2367; Dutch P. 42,557 (1938) to N. V. de Bataafsche Petroleum Maatschappij, *C. A.*, 32, 6778; French P. 809,675 (1937) to N. V. de Bataafsche Petroleum Maatschappij, *C. A.*, 31, 8648.

* For references to table see p. 800.

Table 35—(Continued)

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Table 36—Preparation of Liquid Products (Lubricants or Motor Fuels) by Polymerization of Gaseous or Low-boiling Olefinic Hydrocarbons

U. S. P. 1,309,482 (1919) to R. H. Brownlee; *C. A.*, 13, 2274.
U. S. P. 1,668,328 (1926) to A. M. McAfee (to Gulf Refining Co.); *National Petroleum News*, Feb. 9, 1938, p. R-46.
U. S. P. 1,679,093 (1928) to S. P. Miller and J. B. Hill (to The Barrett Co.); *C. A.*, 22, 3667.

Table 36—*(Continued)*

U. S. P. 1,752,921 (1930) to S. P. Miller (to The Barrett Co.); *C. A.*, 24, 2594.
U. S. P. 1,838,748 (1931) to O. Behimer (to Texas Co.); *C. A.*, 26, 1111.
U. S. P. 1,877,664 (1932) to D. A. Howes (to Imperial Chemical Industries Ltd.); *C. A.*, 27, 187.
U. S. P. 1,898,774 (1933) to R. A. Halloran and M. L. Chappell (to Standard Oil Co. of Calif.); *Brit. Chem. Abs.*-B, 903, 1933.
U. S. P. 1,923,693 (1933) to W. Pungs and H. Rabe (to I. G.); *C. A.*, 27, 5181.
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U. S. P. 1,955,260 (1934) to Standard Oil Co. of Indiana; *C. A.*, 28, 3880.
U. S. P. 1,960,625 (1934) to G. Egloff (to Universal Oil Products Co.); *Brit. Chem. Abs.*-B, 295 (1935).
U. S. P. 1,965,390 (1934) to M. Pier (to I. G. Farbenindustrie).
U. S. P. 1,970,402 (1934) to H. R. Snow (to Standard Oil Co.); *Brit. Chem. Abs.*-B, 759 (1935).
U. S. P. 1,971,301 (1934) to H. Haeuber (to I. G. Farbenindustrie); *C. A.*, 28, 6561.
U. S. P. 2,034,405 (1936) to F. H. MacLaren (to Standard Oil Co.); *Brit. Chem. Abs.*-B, 413 (1937).
U. S. P. 2,040,658 (1936) to Standard Oil Co. of Ind.; *C. A.*, 30, 6768.
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U. S. P. 2,067,030 (1937) to Shell Development Co.; *C. A.*, 31, 1602.
U. S. P. 2,076,201 (1937) to Shell Development Co.; *C. A.*, 31, 3598.
U. S. P. 2,082,500 (1937) to W. E. Kuentzel (to Standard Oil Co. of Ind.); *C. A.*, 31, 5566.
U. S. P. 2,082,518 (1937) to R. F. Ruthruff (to Standard Oil Co. of Ind.); *C. A.*, 31, 5376.
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U. S. P. 2,082,520 (1937) to R. F. Ruthruff (to Standard Oil Co. of Ind.); *C. A.*, 31, 5376.
U. S. P. 2,084,052 (1937) to L. H. Fitch, Jr. (to Phillips Petroleum Co.); *C. A.*, 31, 5376.
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British P. 414,237 (1934) to N. V. de Bataafsche Petroleum Maats.; *C. A.*, 29, 596.
British P. 425,893 (1935) to J. Y. Johnson; *Brit. Chem. Abs.*-B, 441 (1935).
British P. 432,310 (1935) to Standard Oil Development Co.
British P. 448,790 (1936) to Dussek Brothers and Co., Ltd.; *C. A.*, 30, 8437.
British P. 463,468 (1936) to Ruhrchemie; *Brit. Chem. Abs.*-B, 645 (1937).
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British P. 497,541 (1938) Addn. to British P. 466,996, to I. G. Farbenindustrie; *Brit. Chem. Abs.*-B, 125 (1939).
British P. 498,526 (1939) to I. G. Farbenindustrie; *C. A.*, 33, 4351.
British P. 503,306 (1939) to Ruhrchemie A.-G.; *C. A.*, 33, 7093.

Table 36—*(Continued)*

Canadian P. 319,995 (1932) to F. W. Sullivan, Jr., and V. Voorhees (to Standard Oil Co.); *C. A.*, 26, 2586.
Canadian P. 356,807 (1936) to J. F. M. Caudri (to Shell Development Co.); *C. A.*, 30, 3221.
Dutch P. 35,963 (1935) to I. G. Farbenindustrie; *C. Z.*, 1936 *I*, 447.
Dutch P. 36,948 (1935) to N. V. de Bataafsche Petroleum Maats.; *C. A.*, 30, 2743.
Dutch P. 44,471 (1938) to N. V. de Bataafsche Petroleum Maats.; *C. A.*, 33, 3139.
Dutch P. 45,956 to N. V. de Bataafsche Petroleum Maats.; *C. A.*, 33, 8984.
French P. 608,425 (1925) to Braunkohlen-Produkte; *Brit. Chem. Abs.*-B, 245 (1927).
French P. 650,799 (1928) to I. G. Farbenindustrie; *C. A.*, 23, 3341.
French P. 669,793 (1929) to I. G. Farbenindustrie; *C. A.*, 24, 1970.
French P. 679,325 (1929) to I. G. Farbenindustrie; *C. A.*, 24, 3597.
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French P. 695,125 (1930) to I. G. Farbenindustrie; *C. Z.*, 1931 I, 2007.
French P. 712,912 (1931) to I. G. Farbenindustrie, *C. Z.*, 1932 *I*, 477.
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French P. 742,935 (1933) to N. V. de Bataafsche Petroleum Maats.
French P. 761,417 (1934) to N. V de Bataafsche Petroleum Maats; *C. A.*, 28, 4219.
French P. 800,185 (1936) to Standard Oil Co.; *C. A.*, 30, 8597.
French P. 810,155 (1937) to N. V. de Bataafsche Petroleum Maats; *C. A.*, 32, 587
French P. 818,552 (1937) to I. G. Farbenindustrie, *C. A.*, 32, 2652
French P. 820,579 (1937) to Universal Oil Products Co.; *C. A.*, 32, 3129
French P. 835,014 (1938) to N. V. de Bataafsche Petroleum Maats, *C. A.*, 33, 4416
German P. 516,653 (1930) to R. Michel (to I. G Farbenindustrie); *C. A.*, 25, 2845
German P. 540,014 (1931) to I. G Farbenindustrie; *C. A.*, 26, 1770
German P. 546,082 (1932) to M. Pier and F. Christmann (to I. G Farbenindustrie); *C. A.*, 26, 3871
German P. 548,578 (1932) to R. Michel, W. Pungs, and E. Galle (to I. G Farbenindustrie), *C. A.*, 26, 4168.
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German P. 629,762 (1936) to N. V. de Bataafsche Petroleum Maats; *C. A.*, 30, 6182
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G. Egloff, E. Wilson, G. Hulla, and P. M. van Arsdell, *Chem. Rev.*, 20, 345-411 (1937), *C. A.*, 31, 8504 (1937).
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Table 37—Production of Lubricants by Polymerization of Olefins Obtained by Hydrogenation of Carbon Monoxide

C. Berthelot, *Chim. et Ind.*, 37, 1049-1055 (1937); *Brit Chem. Abs.*-B, 869 (1937).
F. Fischer, *Oel u. Kohle*, 11, 120-122 (1935); *J. Inst. Petrol. Tech.*, 21, 170A (1935).
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British P. 454,289 (1935) to Courtis & Co., and F. Johnson; *Brit. Chem. Abs.*-B, 1190 (1936).
British P. 470,534 (1937) to Ruhrchemie A.-G.; *J. Inst. Petrol. Tech.*, 23, 435A (1937).
British P. 504,350 (1939) to Ruhrchemie A.-G.; *C. A.*, 33, 7556.
French P. 792,021 (1935) to Studien- und Verwertungsgesellschaft m.b.H.; *C. A.*, 30, 4314.
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Polymerization of Diolefins with Aluminum Chloride

The author [20] has shown that when a pure diolefin is treated with pure anhydrous aluminum chloride no visible chemical reaction, such as rise in temperature, occurs. This is quite the reverse in the case of olefins which polymerize rapidly with the evolution of heat in the presence of anhydrous aluminum chloride. Upon prolonged standing, diolefins slowly polymerize, and after days or weeks a high molecular weight polymer is

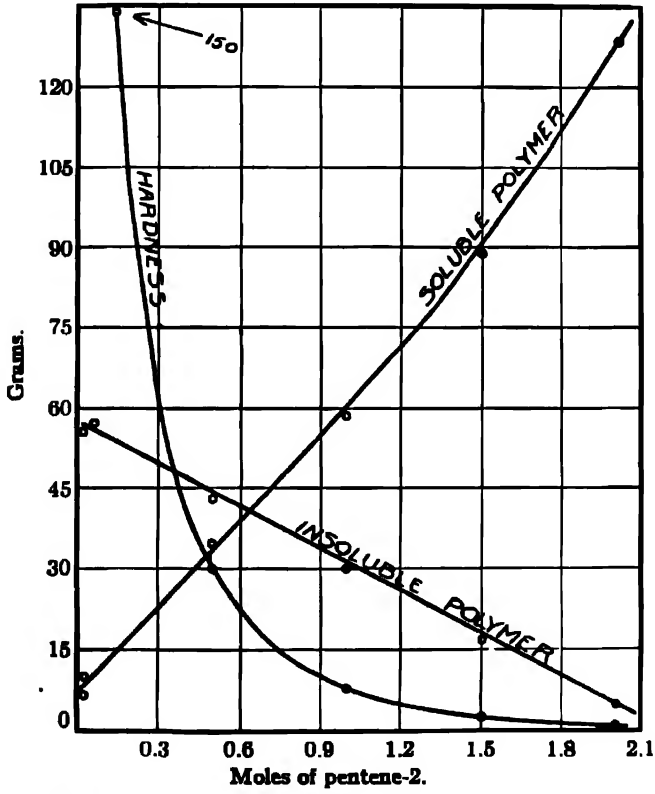


FIG. 5. Yield of soluble and insoluble polymers formed when pentene-2 is varied, keeping isoprene constant at 1 mole. Variation in hardness of soluble polymer. [C. A. Thomas and W. H. Carmody, *J. Am. Chem. Soc.*, 54, 2482 (1932)].

obtained. In this reaction it is exceedingly important that no olefins are present to contaminate the diolefin. The author has studied this reaction mainly with isoprene, which can be obtained readily by the pyrolysis of rubber. Even if the isoprene is subsequently purified by distillation, and washed with ammoniacal cuprous chloride to remove all acetylene compounds, it is still not pure enough. It is necessary to purify the isoprene further by converting to the tetrabromide and regenerating with

[20] C. A. Thomas and W. H. Carmody, *J. Am. Chem. Soc.*, 54, 2480-2484 (1932).
[21] G. S. Whitby and R. N. Crozier, *Can. J. Research*, 6, 206-225 (1932).

zinc dust according to the method of Whitby and Crozier.[21] It is also necessary to wash the anhydrous aluminum chloride with some inert solvent so as to remove completely the hydrogen chloride adsorbed on the surface of the aluminum chloride. It has been shown that even a trace of hydrogen chloride will start the reaction, and if it is allowed to proceed without cooling, the boiling point of the diolefin will soon be reached. By polymerizing isoprene with anhydrous aluminum chloride two polymers are generally obtained, one soluble in most non-polar organic solvents, the other insoluble in all solvents tried. Besides initiating the polymerization of isoprene, hydrogen chloride greatly influences the yield of soluble and insoluble polymers.[22]

The soluble polymer is for the most part $(C_5H_8)_x$, but the insoluble polymer may be of a different structure and certainly is the higher in molecular weight. Isoprene hydrochloride, formed by passing hydrogen chloride into isoprene, reacts with aluminum chloride to form a complex which is soluble in isoprene. This suggests that the soluble polymer is produced in relation to the isoprene hydrochloride present, and that when enough is present to dissolve the aluminum chloride completely, only soluble polymer is produced. This point was further substantiated when it was found that only the soluble polymers were formed when isoprene hydrochloride was added to the reaction mixture of isoprene and aluminum chloride.

Other mutual solvents for isoprene and aluminum chloride increase the yield of soluble and decrease the yield of insoluble polymers. When 5 g of aluminum chloride is dissolved in 45 g of nitrobenzene and this solution added to isoprene, only a soluble polymer is obtained. If a diluent, such as petroleum naphtha, is used with the isoprene, the aluminum chloride is partly thrown out of solution, and some insoluble polymer is obtained. Ethyl acetate forms with aluminum chloride an isoprene-soluble complex; and by running a series of identical polymerizations, with the exception of increasing by small amounts the ethyl acetate added to the reaction mixture, it has been found that there is an exact relation between the yield of soluble polymer and the amount of ethyl acetate added. This relationship is much the same as when pentene-2 is added to isoprene.

If we assume that the soluble and insoluble polymers differ in molecular weight only, it is evident that the more aluminum chloride put into solution, the lower the molecular weight of the polymer obtained. When no mutual solvent for the isoprene and aluminum chloride is present, polymerization is initiated on the surface of the catalyst. With solid aluminum chloride the surface is exceedingly small when compared to the same mass of aluminum chloride in solution as a complex. Thus, with a solid piece of aluminum chloride in isoprene, not many polymer growths are started, and after prolonged contact the polymers have an opportunity

[22] C. A. Thomas and W. H. Carmody, *J. Am. Chem. Soc.*, **52**, 3354-3356 (1930).

to grow to large size and become insoluble. When a catalyst is in solution so that molecular contact is effected, many polymer growths are started, and these are so numerous that with the available isoprene they do not grow to high molecular weights. Soluble polymer is thus produced. This theory of short chain formation has been independently advanced by Houtz and Adkins [23] in their work on styrene. Further substantiating the foregoing evidence, it is interesting to note that when anhydrous aluminum chloride is very finely ground and placed with isoprene considerably less insoluble polymer is formed than when coarse aluminum chloride is used. Here again with the finely divided catalyst the greater amount of surface which is exposed initiates more polymer growth.

Thus, it can be seen that solvents play an important part in the polymerization with anhydrous aluminum chloride. If the aluminum chloride reacts with the solvent, an entirely different catalytic effect will be obtained. Listed below are some of the diluents tried in this laboratory for anhydrous aluminum chloride:

Carbon disulfide	Toluene
Carbon tetrachloride	Xylene
Chloroform	Halowax
Ethylene chloride	Petroleum ether
Ethylene bromide	Ligroin
Benzene, C. P.	Methyl alcohol
Benzene, Tech.	Diethylene glycol
Gasoline	"Cellosolve" acetate
Varnoline	Butyl "Cellosolve"
Benzonitrile	"Carbitol"
Phenylcyclohexane	Dichloroethyl ether
Nitromethane	Butyl "Carbitol"
Ether	Methyl "Cellosolve"
Alcohol	Acetone
Nitrobenzene	"Cellosolve"
Amylbenzene	Ethyl acetate

Carmody [24] has shown that isoprene will polymerize totally to a soluble polymer if its vapors come into contact with aluminum chloride.

The polymerization of a diolefin, such as isoprene, with anhydrous aluminum chloride, lends itself to many speculations, particularly to the fact that there seems to be an evolution of hydrogen chloride gas from the isoprene during polymerization. This could be explained on the following basis [25]:

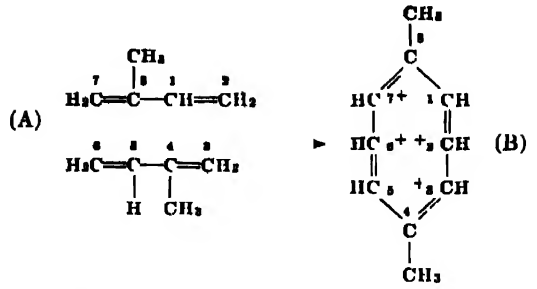
Two moles of isoprene treated with aluminum chloride may join as follows:

[23] R. C. Houtz and H. Adkins, *J. Am. Chem. Soc.*, 55, 1609-1617 (1933).

* See p. 24 for solubility data of aluminum chloride in these and other solvents.

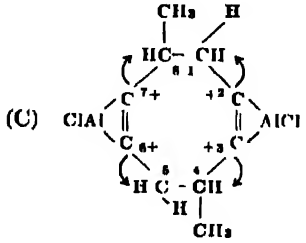
[24] W. H. Carmody and M. O. Carmody, *J. Am. Chem. Soc.*, 59, 2073-2074 (1937).

[25] W. H. Carmody, Investigation made at Thomas and Hochwalt Laboratories.



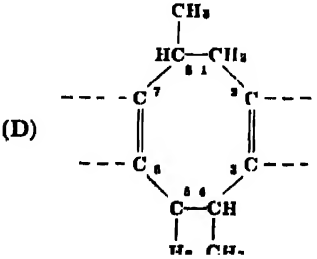
Carbon atoms 2, 3, 6, and 7 each lose one hydrogen atom in the presence of aluminum chloride which escapes as bubbles of hydrogen chloride.

This octahedron is no longer $(C_5H_8)_2$ but now becomes $(C_5H_6)_2$ and this is the unit which undergoes polymerization under the further influence of aluminum chloride according to the scheme shown below.



Under the influence of further aluminum chloride, the tetraene rearranges with the formation of an aluminum complex. Carbon atoms 2, 3, 6, and 7 lose hydrogen by migration to carbon atoms 1, 4, 5, and 8.

The aluminum chloride loses chlorine as hydrogen chloride simultaneously with the formation of (B). The aluminum chloride residue immediately combines to form complex (C) which is the active unit of polymerization.



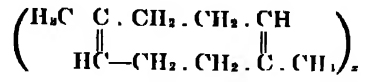
The aluminum complex undergoes further degradation at carbon atoms 2, 3, 6, and 7 and the diene (D) is in an active state to combine with other (D) units

The evidence for this theory is interesting. Thus, the insoluble polymer obtained by polymerization of isoprene free from any impurities may have the formula $(C_5H_6)_x$; this polymer should be a cycloöctadiene polymer linked together by a series of cyclobutadiene rings. It has been pointed out that any olefin, such as amylene, added to isoprene during polymerization with anhydrous aluminum chloride will reduce the amount of

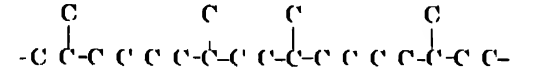
insoluble polymer formed. The optimum ratio of amylene added is 2:1, and at this ratio there is enough olefin present to absorb all the hydrogen chloride produced by the isoprene in contact with the aluminum chloride.

According to Pickles,[26] the polymerization of isoprene into rubber must be accompanied by a rearrangement of the double bonds.

A cyclic polymer has been advanced by Harries[27]:



In a series of investigations dealing with sodium rubber, Midgley and Henne[28] found no trace of compounds of a cyclic nature. Their results, together with studies dealing with products of the destructive distillation of sodium rubber, indicated the following carbon arrangement for sodium rubber:



Bromine titration indicated one double bond for each C_5H_8 unit.

Co-polymerization of Diolefins with Olefins in the Presence of Aluminum Chloride

It has been shown that diolefins and olefins react in the presence of anhydrous aluminum chloride to form two polymers, one soluble and the other insoluble in hydrocarbon solvents. Generally the amount of soluble polymer formed is a function of the olefins present; the more olefins in the mixture, the more soluble polymer formed. The hardness and molecular weight of the resulting polymer is inversely proportional to the amount of olefins present and the amount of insoluble polymer is an inverse function of the olefin present.

Later[29] it was shown that the function of the olefin is merely to solubilize the aluminum chloride, and that other compounds, such as a solvent or hydrogen chloride, act in the same capacity. The resins formed by polymerization of olefins and diolefins are hemi-colloids having a molecular weight from 300 to 2000 depending upon the amount of olefins, the type of olefins, and the amount of diolefins and the type of diolefin employed. They range from viscous oils to hard, brittle, pliable resins, with a melting point as high as 150°.

From the foregoing discussion it should be pointed out that not only do straight-chain olefins and diolefins co-polymerize with anhydrous aluminum chloride, but that the reaction is applicable to other combinations. There may be used cyclic olefins with straight-chain diolefins, cyclic

[26] S. S. Pickles, *J. Chem. Soc.*, 97, 1085-1090 (1910).
[27] C. Harries, *Ann.*, 383, 157-227 (1911).
[28] T. Midgley and A. L. Henne, *J. Am. Chem. Soc.*, 51, 1294-1296 (1929); 52, 2077-2078 (1930); 54, 381-386 (1932).
[29] C. A. Thomas and W. H. Carmody, *J. Am. Chem. Soc.*, 55, 3854-3856 (1933).

diolefins with straight-chain olefins, or cyclic diolefins with cyclic olefins. The following table gives a partial list of some of the compounds studied in this laboratory:

Table 38

Substance and Fraction	(cc)	Catalyst (g/100 cc)	Yield of resins g/100 cc of active material taken	Iodine No	Remarks
Cyclohexene Isoprene Heptane	50 50 150	3 5	30 9	....	Extremely hard, glassy, high m p , no tackiness even when softened. Brownish amber color.
1-Methylcyclohexene Isoprene Heptane	50 50 150	3 5	31 5	....	Dark red soft resin Resem bling tar, flows in cold
Methylcyclohexene Isoprene	27 26	9 1	48 2	144 0 147 0	Soft resin- dark brown color
Isoprene Cyclohexene	91 91	5 5	47 1 mix	132 0 130 0	Very hard clear, brittle pale amber color with brownish tinge
Cyclohexene Isoprene Xylene	40 40 150	4 4	17 3 mix 49 4 cyclohexene and isoprene	70 8 71 3	Hard, clear, brittle, dark brown amber
Cyclohexene Isoprene Toluene	40 40 150	4 4	22 2 mix 64 0 cyclohexene and isoprene	87 7	Hard, clear, brittle, very slightly tacky, brilliant amber yellow
Cyclohexadiene	35	2 0	37 0	130 3 131 3	Very hard, clear, brittle, pale amber yellow
Cyclohexadiene Cyclohexene	23 25	2 0	19 8 mix 41.3 hexadiene	115 9 114 6	Very hard, clear, brittle pale amber yellow.
Cyclohexadiene Pentene-2	23 26	2 0	15 1 mix 32 2 hexadiene	147 8 148 2	Very hard, clear, brittle pale amber yellow
Cyclohexadiene Toluene	23 27	2 0	18 4 mix 40 0 hexadiene	111 3 110 6	Very hard, clear, brittle pale amber yellow

Co-polymerization of Diolefins with Aromatic Compounds in the Presence of Anhydrous Aluminum Chloride

It has been found that diolefins react with substituted aromatic hydrocarbons—a reaction which is similar to that of a combination of olefins with aromatic hydrocarbons.* As it is impossible to remove the catalytic complex, the intermediate products from the condensation of diolefins with aromatics continue to polymerize to resin. Here again two polymers are formed, a soluble and an insoluble one. When studying pure compounds in this type of reaction it has been found that the more substituted the aromatic nucleus, the greater is the tendency for the reaction to take place. In fact, no appreciable amount of resin is formed from a diolefin and pure benzene. Some general observations are of interest in the case of isoprene with various substituted aromatics.

Xylene is the simplest di-substituted benzene containing two methyl groups. When the three xylenes are respectively polymerized with a diolefin, such as isoprene, the *para*-xylene yields the smallest proportion of resin. It has the highest melting point and is lighter in color than that obtained from either *ortho*- or *meta*-xylenes, which produce higher yields of resin of a darker color. When the methyl groups in xylene are replaced

* See Chapter 8.

by higher molecular weight alkyl groups, the yield of resin is greater and the color is lighter. The more branched the chain in the alkyl substituent, the more noticeable is this effect. This reaction takes place with cyclic diolefins as well as straight-chain diolefins. In the case of the cyclic compounds it is much more vigorous and the resulting resin is harder and of a better character.

Synthetic Resins from Cracked Petroleum Distillate

Petroleum cracked under severe conditions presents a convenient and logical raw material for the production of synthetic hydrocarbon resins by polymerization with anhydrous aluminum chloride. A medium of highly cracked distillate offers the opportunity for the polymerization of olefins, the combination of olefins with aromatics to form substituted aromatics, the polymerization and condensation of diolefins and olefins to form resin, and the combination of diolefins with substituted aromatics and subsequent polymerization of this intermediate product to resin.

In the manufacture of resins from cracked petroleum distillates rigid specifications are maintained upon the cracking operations and upon its products. Boiling range, specific gravities, refractive index, and average molecular weight are some of the determinations made upon each sample of the distillate produced. The composition, that is, the content of aromatic, mono-olefin, and diolefin hydrocarbons, is determined by the usual method. If a particular distillate fails to meet the required specifications it can be blended with other distillates, or its deficiencies can be corrected by the addition of various substances; for example, if the content of mono-olefin is low, a definite amount of amylene or other mono-olefin can be added. During the polymerization of such a distillate with anhydrous aluminum chloride, all four reactions probably take place simultaneously, as outlined above.

For the production of a hydrocarbon resin known to the trade as "Santo-Resin," polymerization is carried out in vessels equipped for adequate cooling, since the reaction is highly exothermic; and the anhydrous aluminum chloride is added in a finely divided state in a small, continuous, controlled stream. The distillate darkens as polymerization continues and has a dark reddish brown color at the end of the reaction. The specific gravity of the distillate increases as polymerization continues; thus by determining the specific gravity of the reaction product, the degree of polymerization can be ascertained. When the reaction is completed, no further rise in specific gravity occurs even upon further addition of catalyst. The reaction mixture is then treated with a suitable alkali to break down the aluminum chloride complex while the hydrocarbons still remains in solution. Since in the manufacture of resinoids highly viscous liquids are formed, in some cases it has been found that the aluminum chloride complex can be broken down more readily by adding a solution of ammonium hydroxide in ethyl or propyl alcohol. The alcohol serves to bring the alkali into intimate contact with the nonpolar solvent and resinoids in solution. On the addition of alkali, alu-

minum hydroxide and alkali chloride are precipitated, together with a small amount of the insoluble polymer.

The relative yield of soluble and insoluble polymer may be governed by the raw material used. The inorganic material is separated from the resin in solution by filtration. By repeatedly treating the solid residue with dilute acid and subsequently washing out the inorganic salt, there is left a white granular insoluble polymer. The soluble polymer left in the filtrate is recovered by removing the solvent by distillation at as low a temperature as possible. Vacuum distillation is usually employed. The last traces of high-boiling oils are removed by passing superheated steam directly into the hot molten resin. Up to certain limits the hardness of the resin is controlled by means of this addition of superheated steam. The melting point of the resin produced by this process can be varied according to the use to which the product is subjected; it usually ranges from around 100 to 150°.

Resins of this nature, which are hemicolloids, usually find a commercial outlet in varnishes.[30] It has been found that the drying rate of Chinawood oil varnishes is largely dependent on the type of resin used and on its preparation.[31] Boiled varnishes made with neutral resins dry faster than those made from acid resins; and since hydrocarbon resins are generally neutral, they give very fast-drying varnishes. Because of their hydrocarbon nature these resins are highly resistant to alkali, water, and acid. Some resins produced by polymerization of hydrocarbons undergo gelation when heated with Chinawood oil, and it is not definitely known whether or not this is a truly chemical reaction between resin and oil. However, the resulting varnish seems to be more durable when gelation occurs in the varnish manufacture. This is readily explainable on the basis that a resin of low molecular weight, around 1000 to 1500, will not in itself form a durable film; but such a hemicolloid, when cooked with a drying oil, such as Chinawood oil or linseed oil, seems to form a composite which is quite durable.

Resins of higher iodine value can be obtained by controlling the polymerization, but usually the resulting polymer is slightly lower in molecular weight. This resinoid of high iodine value resembles a drying oil.

Polymerization of Aromatic or Heterocyclic Unsaturated Compounds with Aluminum Chloride

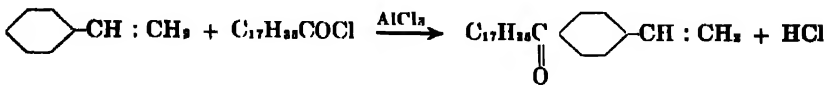
In the polymerization of styrene, the use of aluminum chloride causes the formation of lower polymerization products having a molecular weight of 30,000 or less. These are brittle and have a low softening point.[32]

[30] U. S. P. 2,039,366 (1936) to C. A. Thomas (to Dayton Synthetic Chemicals, Inc.), *C. A.*, 30, 4344; U. S. P. 2,039,364 (1936) to C. A. Thomas and C. A. Hochwalt (to Monsanto Petroleum Chemicals, Inc.), *C. A.*, 30, 4344; U. S. P. 2,039,365 (1936) to C. A. Thomas (to Monsanto Petroleum Chemicals, Inc.).

[31] C. A. Thomas and P. E. Marling, *Ind. Eng. Chem.*, 24, 871-873 (1932).

[32] Anon, *British Plastics*, 9, 477-478 (1938).

According to Ralston,[33] flexibility may be imparted by first reacting styrene with a high molecular weight aliphatic acid chloride:



Polymerization of the acylated product by heat or catalysts yields flexible resins. Acylation of other resin-forming compounds, for example, coumarone, indene, dicyclopentadiene, or phenol may be similarly effected.[34] It has been shown in this laboratory that such low molecular weight resins produce flexible but slightly tacky films.

Aluminum chloride catalyzes the polymerization of indene. The products are similar to those formed by the action of concentrated sulfuric acid, but reaction is slower.[35] The use of aluminum chloride as a polymerizing agent for unsaturated hydrocarbons derived from coal tar is frequently reported.*

A summary of literature dealing with the production of resins by aluminum chloride polymerization of unsaturated hydrocarbons is given in Table 39, page 812.

Preparation of Drying Oils

Under certain conditions the treatment of a mixture of olefins and diolefins with aluminum chloride results in production of drying oils. Mikeska and Gleason[36] contact a mixture of cracked hydrocarbons boiling below about 205° and containing olefins and diolefins with aluminum chloride at about 38°, and obtain a benzene- and acetone-soluble liquid, boiling at 205°/2 mm, which has drying properties.

In another process, a liquid product obtained from a vapor-phase cracking process and having a considerable proportion of diolefins is treated at temperatures of not over 70° with 1 per cent or less by weight of aluminum chloride.[37] The drying oil may be isolated by separating the polymerized oil from the sludge formed in reaction, neutralizing it and subjecting it to a non-cracking distillation to form a residue in which the drying components are concentrated.[38]

A drying oil has been produced by treating with aluminum chloride a cracked gasoline fraction (b.p. 27-84°) of the following composition:

butenes and butadiene	15.0 per cent
hexenes and benzene	14.5 per cent
pentenes and isoprene	52.0 per cent

(*Text cont'd. on p. 814*)

[33] A. W. Ralston, *Oil and Soap*, 16, 215-218 (1939).
[34] A. W. Ralston, R. J. Vander Wal, S. T. Bauer, and E. W. Segebrecht, *Ind. Eng Chem.*, 32, 99-101 (1940).
[35] H. Stobbe and E. Farber, *Ber.*, 57, 1838-1851 (1924), *C. A.*, 19, 492.
* See page 813.
[36] U. S. P. 2,092,889 to L. A. Mikeska and A. H. Gleason (to Standard Oil Development Co.).
[37] French P. 791,739 (1935) to N. V. de Bataafsche Petroleum Maatschappij, *C. A.*, 30, 4344.
[38] Canadian P. 360,536 (1936) to H. I. Waterman (to Shell Development Co.), *C. A.*, 30, 7835.

Table 39.—Polymerisation of Olefinic or Diolefinic Hydrocarbons, with or without Addition of Aromatic Hydrocarbons for Formation of Resinous Products

Hydrocarbon	Ref.
Gaseous Olefins (+blowing the polymer with air)	46
Allene	55
Butadiene (slow polymerisation)	22
Butadiene-Na polymer (hardened by treatment with $AlCl_3$)	55
1,4-Cyclohexadiene	22
Cyclopentadiene (only little polymerisation)	14
Diolefins	4
2,3-Dimethylbutadiene	22
Isoprene	22
Isoprene (in benzene)	3
Isoprene (in pentene-2)	18, 19
Isoprene	6
Still residues from preparation of synthetic rubber	80
Pine oil (to yield a dipolymer)	26
Dipentene (to yield a dipolymer)	25
Terpenes (or a mixture of terpenes)	30
Turpentine	29
Turpentine oil	13
Wood tar	13
Olefin+diolefin (*e.g.*, amylene+isoprene)	39
Olefin+diolefin (cracked distillate, b. 30-40°)	37
Olefin+diolefin (molding)	44a
Olefin+diolefin (cracked distillate, b. 30-40°+hydrogenation)	44
Butadiene+hexene	67
Olefin+diolefin	75
Isoprene+amylene, or pinene, or camphene	1
Butadiene+olefins	22
Diolefin+olefin	51
Conjugated diolefin+olefin	66
Diolefin+olefin (*e.g.*, butadiene or isoprene+isobutene, propene or cracked paraffin)	74
Diolefin+substituted benzene (*e.g.*, isoprene+alkyl benzene)	31
Diolefin+alkyl benzene (*e.g.*, butadiene or isoprene+toluene)	70
Conjugated diolefin+alkyl benzene (*e.g.*, butadiene+toluene)	66
Diolefin+cyclic hydrocarbons (*e.g.*, butadiene+tetrahydronaphthalene, benzene, *m*-xylene, chlorobenzene, or nitrobenzene)	56
Mixture of terpene with alkyl benzene	30
Cracked distillate contaming 45-60% of unsaturated hydrocarbons	5, 9 17
Cracked petroleum distillate (b.p. below 180° containing olefins, diolefins, and alkyl benzenes)	27 37 65 68, 78
Cyclic hydrocarbon having at least one double bond, an unsaturated hydrocarbon of a different degree of unsaturation, and an alkyl benzene (*e.g.*, cyclohexene, isoprene, and toluene)	32
Straight-chain olefins and diolefins (cracked distillate b. 25-50°)+polymers of cyclic diolefins, cyclic olefins, straight-chain olefins, and alkyl benzenes (distillate b 125-180°)	33
Cracked distillate, b. 30-160° (neutralisation of catalyst with NH_3 in EtOH+C_6H_6)	37
Cracked distillate, b. 30-160°+subsequent reaction with polyhydric alcohols	35
Cracked distillate, b. 30-160°+subsequent reaction with drying oil	41, 69
Cracked distillate, b. 30-160°+presence of a material which is inert and hygroscopic and capable of removing HCl	49
Cracked distillate, b. 30-160°+sulfuric acid and clay for decolorization	47
Cracked distillate, b. below 200° (catalyst neutralised with caustic alkali)	45b
Cracked distillate, b. below 200° (catalyst neutralised with a suspension of an alkaline-earth hydroxide in a mixture of water with water soluble alcohols or ketones)	48
Cracked distillate, b. 120-180°	36
Light oil, b. 43-246° (containing olefins, diolefins, and substituted aromatic hydrocarbons) (gave 19-20% resins)	10-12
Cracked gas oil distillate, b. 25° (80% b. at 110°) (gave 30-40% yield resin)	20
Liquid hydrocarbons obtained by cracking products from hydrogenation of carbonaceous material	72
Gasoline b. up to 210° (with C_2H_4-$AlCl_3$ complex as catalyst)	61, 71
Cracked distillate obtained from a charging stock consisting of petroleum hydrocarbons +an aromatic hydrocarbon	45
Liquid SO_2 extract of naphtha containing unsaturates and aromatics	50a
Liquid hydrocarbons produced in the pyrolysis of normally gaseous hydrocarbons	51b
Cracked distillate, b. 30-220°+acetylene	45a
Conjugated double bond (Diolefin+olefinic hydrocarbons+aromatic hydrocarbons; subsequent oxidation of polymer)	50
Olefins, diolefins, and acetylenes, *e.g.*, cracked petroleum gases+hydroformed naphthas	63
Styrene+isobutene+cracking distillate	61
Naphthalene-unsaturated hydrocarbon-tar mixture-fraction b. 180-300°/1-10 mm (naphthalene is recovered)	51a
Petroleum residues	81
Petroleum tar	60
Petroleum asphalt	50
Petroleum tar distillate	59, 31b, 28b
Petroleum tar distillate	36 42b
Cracked tar and petroleum pitch	34
High boiling petroleum residues (b. 149-349°)	70
Dehydrogenated solid or semi-solid paraffin hydrocarbons	77

Table 39—*(Continued)*

Hydrocarbon	Ref.
Cracking oil tar	42
Chlorinated distillate from cracking oil tar	38
Low melting coal tar distillates	76
Coal tar distillate	54
Tars or asphalts	52
Indene (to di-indene)	10
Coumarone	7
Coumarone oil	15
Solvent naphtha containing coumarone and indene	24,53
Coumarone and indene of crude aromatic hydrocarbon fraction	28
Purified coal tar naphtha	8
Purified naphtha distillate of coal tar	29
Coal tar oil containing coumarone-indene (in presence of dissolved unvulcanized rubber)	62
Tetrahydronaphthalene (polymerization to oils containing anthracene or phenanthrene derivatives)	30
Benzil (to compounds having 5-20.5 moles)	2

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40. U. S. P. 2,039,365 (1936) to C. A. Thomas (to Monsanto Petroleum Chemicals, Inc.); *C. A.*, 30, 4344.
41. U. S. P. 2,039,367 (1936) to C. A. Thomas (to Monsanto Petroleum Chemicals, Inc.); *C. A.*, 30, 4227.

Table 39—*(Concluded)*

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Upon treatment of the fraction with 1.5-2 per cent of aluminum chloride at 10-20° for three to four hours a high molecular oil was obtained in 50 per cent yield. To this oil 35-40 per cent of a solvent is preferably added to secure sufficient fluidity.[39]

Drying oils from gasoline have also been prepared by treating gasoline with aluminum chloride and hydrogen chloride at 100-120° for four hours.[40]

Miscellaneous Aluminum Chloride-catalyzed Condensations Leading to High Molecular Weight Products

The tendency of mono-olefins to undergo polymerization is greatly increased by the introduction of an electronegative group at one of the

[39] I. Pototovskii, A. Atal'yan, and V. Buinitskaya, *Azerbaidshanskoe Neftyanoe Khozyaistvo*, No 10, 91-97 (1934); *C. A.*, 29, 6080.
[40] Russian P. 39,809 (1934) to S. L. Varshavskii and I. K. Shenfinkel; *C. A.*, 30, 3668.

carbon atoms of the ethylenic group.[41] The so-called vinyl compounds of the type CH_2:CHR, in which R is a negative group, for example, vinyl halides, vinyl ethers, and vinyl esters, are writing an ever-growing chapter in the field of plastics and resins. Aluminum chloride is little used for effecting polymerization of unsaturated vinyl compounds alone. When an olefin containing an electronegative group, such as chloride, is treated with aluminum chloride, not only polymerization but also condensation with the solvent takes place; the resulting polymer is very complex and usually of low molecular weight.[42]

The polymerization of di- or polyhalogenated aliphatic hydrocarbons by means of aluminum chloride leads to formation of resins, or to products which find use as dielectrics. When reaction is effected in the presence of aromatic hydrocarbons or their halogenated derivatives, products are obtained which appear to be polymers of arylated olefins.* Arylalkyl halides react as do olefinic dihalides with aromatic hydrocarbons.

Friedel and Crafts[43] noted that benzyl chloride was converted upon treatment with aluminum chloride into a polymeric product which was extremely insoluble; and Jacobson[44] reports the formation of insoluble hydrocarbon, $(C_7H_6)_x$ and a small amount of a soluble resin having the same empirical formula. The molecular weights of the soluble resin varied from 1260 to 2250. The resin is obviously produced by a linear Friedel-Crafts autocondensation:

$$C_6H_5CH_2Cl \qquad C_6H_5CH_2C_6H_4CH_2Cl \qquad C_6H_5CH_2(C_6H_4CH_2)_nC_6H_4CH_2Cl$$

Condensation of ethylene dihalides with aromatic hydrocarbons may proceed, in the presence of aluminum chloride, to give a class of elastic plastic materials known as AFX. Aromatic hydrocarbons with only one carbon atom in the side chain, such as toluene or xylene, do not undergo the reaction. The polymer has been assumed to be composed of $H_2C.C_6H_4.CH_2$ or $(H_2C)_2.C_6H_2.(CH_2)_2$ units, *sym*-diphenylethane having been isolated as a product from the earliest stages of the reaction.[45]

The production of plastic materials by reaction of mono- or polyhalogenated aliphatic or arylalkyl hydrocarbons with benzene or substituted benzenes is the subject of many patents.*

The following table has been compiled in order to show the wide miscellany of polymerizing condensations to which aluminum chloride has been applied. In reactions involving condensations with cleavage of water, aluminum chloride acts as a dehydrating agent, and is generally suggested only as an optional catalyst.

[41] See G. M. Kline and N. L. Drake, *J. Res. Nat. Bureau Standards*, 13, 705-712 (1934), for a discussion of polymerisation mechanism based upon the theories of free radicals and electronegatives.
[42] *Cf.* H. I. Waterman, J. J. Leendertse, and P. J. G. Colthoff, *Chem. Werkblad*, 32, 550-553 (1935).
* See Table 40.
[43] C. Friedel and J. M. Crafts, *Bull. soc. chim. (2)*, 43, 53 (1885).
[44] R. A. Jacobson, *J. Am. Chem. Soc.*, 54, 1513-1518 (1932).
[45] S. D. Shinkle, A. E. Brooks, and G. H. Cady, *Ind. Eng. Chem.*, 28, 275-280 (1936).

Table 40. Miscellaneous Condensations and Polymerisations Leading to High Molecular Weight Products

Reactants	Product	References
Halogenated Compounds		
Trichloroethylene	resin	
Halogenated olefins	oils and resins	
Polymerized vinyl chlorides	higher polymers	106
Vinyl chloride+toluene as solvent	resin (50%)	9, 14
Halogenated olefins, *e.g.*, trichloroethylene, di- or tetrahalogenated ethylene, or halogenated propylene or butylene	product useful for dielectrics	62
Ethylene chloride+xylene	lubricants and resins	95
Ethylene dihalide and aromatic compounds or halogenated aromatic	resins	2, 12, 57, 70, 75, 81, 89 89a, 87
Vinylidene chloride+aromatic hydrocarbon or halogen-substituted aromatic hydrocarbon		37
2-methyl-3-chloropropene+benzene	resins	94
Naphthalene, xylene, or phenols with naphthalene- or acetylene tetrachloride	resin	17
Hydrocarbon containing halogenated aliphatic carbon atoms (trichloroethylene, ethylene dichloride, methylene chloride, propylene dichloride, or benzyl chloride) and a nuclearly halogenated aromatic hydrocarbon	plastic masses	38
Naphtha fraction, b. 125-500°F.+ethylene dichloride	resin	41 79
Olefins or olefinic cracking gases+halo-substituted diolefins (*e.g.*, chloroprene)	additives to lubricants	72
Olefinic halides+benzene or alkylated or chlorinated benzene	viscous oil or resin	38a, 38b
Propylene chloride or ethylene chloride+benzene	resin	33
An ethylene dihalide+benzene or benzene homolog except methyl benzenes	resin	50
Ethylene dichloride and a partially halogenated benzene	products for electrical insulation	27
Sludge resulting from refining a hydrocarbon oil with aluminum chloride+chlorine or a chlorinated aliphatic hydrocarbon		20
Petrolatum+chlorinated volatile hydrocarbon	resin	30
Partially chlorinated mineral hydrocarbon oil	lubricant	22, 32, 38c 47, 52, 102
Chlorinated paraffinic or olefinic hydrocarbons	polymer, mol. wt. 1200	80a
Benzyl chloride	resin, mol. wt. 1200-2250	5
Benzyl chloride	resin	3, 13
p-Bromobenzyl chloride	resin, mol. wt. 1300-1500	5
Halogen addn. products of naphthalene or hydrogenated naphthalene	resins	96
Aralkyl halide+partially hydrogenated aromatic hydrocarbon	resin	53, 101
Aralkyl halide or halogenated hydrogenated naphthalene+aromatic hydroxycarboxylic acid (*e.g.*, dimethylbenzyl chloride and salicylic acid)		55
Benzyl chloride+rubber	benzylidene rubbers	6, 7, 103
Arylated olefins+chlorine	resins	107
Coumarone-indene tar fraction or low melting coumarone resin+halides of higher aliphatic acids	additives to lubricants	9a
Acetylene		
Acetylene	$7(C_{10}H_{14-8})$, $2Al_2Cl_6$ yielding a light yellow powder and $7(C_{20}H_{18})$.-Al_2Cl_6, a nonvolatile, black sublimate	

Table 40—*(Continued)*

Reactants	Product	References
Acetylene+tar-oil hydrocarbons b. above 140° or mesitylene or pseudocumene	viscous oils	16, 43, 44
Acetylene+acid+hydrocarbons or halogenated hydrocarbons		21
Acetylene+mineral oils containing aromatics	oils or resins	34, 68, 80
Acetylene+aliphatic or cyclic hydrocarbons	resins	42, 81a
Acetylene+mixture of olefins	high molecular weight hydrocarbons	46
Acetylene+mineral oils	oils and brown resins	78
Acetylenic polymer+aromatic hydrocarbon	additive to lubricants and greases	64
Vegetable Oils and Natural Resins		
Drying oils, semi-drying oils or fat acids	polymerized products	67
Fatty oils	lubricants or additives to lubricants	77
Castor oil+HCl (+oxygenation after treatment with $AlCl_3$)	lubricating oil, soluble in water	19, 45
Olive oil	lubricants	11
Cashew nut shell oil	resins	71
Soy-bean oil+HCl or moisture	polymerized product	4
Chinawood oil	moldable product	15
Vegetable oil; *e.g.*, tung oil	product for plasticizing phenol-aldehyde resins	31
Rapeseed oil (+sulfurization after polymerization)	extreme pressure lubricant	93
Shellac	cured product	10
Natural resin+aromatic hydrocarbon	arylated resin	26, 76
Crude abietic acid+aromatic hydrocarbons	resins	61
Natural resins or their esters or acids+solvent	condensation products, more saturated and of higher mol. wt. and m.p.	56, 86
Miscellaneous Condensations and Polymerizations		
Polyvinyl esters, alcohols, or ethers (for higher degree of polymerization)	elastic, more or less infusible products	48
Vinyl ethers	polymerization products	3, 54, 85, 100
Vinyl ethers+SO_2	products which give dyes of high mol. wt. upon coupling with diazo solutions	35, 65
Vinyl compounds+esters of unsaturated high molecular fatty acids	mixed polymers	88
Vinyl compounds+alkyl halides (vinyl ethers or styrene)	constituents of high pressure greases	74
Polyvinyl alcohol+aldehydes	artificial rubber-like masses	83
Vinyl esters+hydroxy-aromatic compounds	artificial materials	82
Vinyl alcohols or hydroxystyrenes+α-haloalkyl ethers or vinyl ethers	resins	58
Cracked petroleum fraction+formaldehyde	resins	28
Halogenated anthracene or phenanthrene+aldehydes	resinous products	
Salicylic acid+formaldehyde	polymerization products for improving skins and furs	92
Aldehyde-amine condensation product+formic acid	resin	29
Rubber+phthaloyl chloride or other oxygenated organic compounds except aldehydes	products resisting abrasives	51, 84, 104
Phenol+sulfur dichloride	resins	60
Phenol+benzotrichloride	resins	30

Table 40—*(Continued)*

Reactants	Product	References
Phenols+halogenated terpenes (*e.g.*, techn. dipentene+HCl+phenol)	oily or resinous products	68, 90, 91
Phenols+isoprene+HCl	resinous products	69
Phenols+vinyl esters+oils	resins	50
Phenols+halogenated naphthalenes or halogenated hydrogenated naphthalenes	resinous products	97
Phenol+acrolein	resins	8, 105
Furfural	resinous products	18
Carbazole or derivatives+olefin (propylene, cyclohexene)	oils or resins	23, 24, 49
Higher aliphatic nitriles (saturated or unsaturated)	viscous oils	39, 40, 73

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Chapter 19

Anhydrous Aluminum Chloride in the Petroleum Industry

The importance of anhydrous aluminum chloride in the petroleum industry is due to its catalytic effect on hydrocarbons involving decomposition, polymerization, alkylation, and isomerization. The practical application of reactions of these types to the petroleum industry is expressed in the following scheme:

Decomposition	Preparation of gasolines by cracking high-boiling hydrocarbons Refining by decomposition of organic compounds of sulfur
Polymerization	Preparation of lubricants and motor fuels by polymerization of low-boiling hydrocarbons Refining by polymerization of gum-forming constituents
Alkylation	Preparation of motor fuels by alkylation of paraffins with olefins Synthesis of pour-point depressants by alkylation of aromatics with higher olefins or alkyl halides
Isomerization	Preparation of branched paraffins having high anti-knock value Ring closure of aliphatic hydrocarbons to confer increased aromaticity

Of the four reactions, isomerization has been the least studied. The isomerizing activity of aluminum chloride, however, is of potential interest in such reactions as in the preparation of isooctane from *n*-butane through isobutane, and in the recognized increase of anti-knock values of gasolines with increasing aromaticity.

Since in the petroleum industry aluminum chloride has been most widely applied in cracking, refining, and in the preparation of pour-point depressants, this chapter will be limited to these fields. Its use in the preparation of polymer lubricants and motor fuels has been discussed in Chapter 18, and its activity as a catalyst for aliphatic alkylations and isomerizations in Chapter 17.

Decomposition of Aliphatic Hydrocarbons

The basis of the use of aluminum chloride in cracking processes depends primarily upon the ability of this reagent to split long-chain hydrocarbons into shorter molecules, thus increasing the yield of gasoline obtainable from crude oils.

The mechanism of the aluminum chloride-catalyzed decomposition of pure aliphatic hydrocarbons has not been studied very intensively; with a few exceptions practically all the data have been reported after the catalytic cracking operation became a commercial success. Since some insight into the nature of the probable reactions can be obtained from

the study of these pure substances, this work will be presented before proceeding to the large-scale processes.

Methane at 250-500° in the presence of aluminum chloride has been reported to show no tendency to form other hydrocarbons, producing only carbon and hydrogen,[1] although it has also been stated that the presence of catalyst promotes the formation of ethylene as well as carbon and hydrogen from methane.[2]

Jurkiewicz and Kling [1] studied the decomposition of the paraffins from methane to isobutane in the presence of aluminum chloride and found that ethane showed some oily product at 320°, but that only carbon was formed at 500°. Propane decomposed more readily than ethane, and at 245° isobutane formed some oil. It was observed in these experiments that above the critical temperature of aluminum chloride, 370-390°, the catalyst showed only a cracking effect, and that the resistance to decomposition decreased with an increase in molecular weight.

Ipatieff and Grosse [3] investigated the action of aluminum chloride on butane, hexane, heptane and 2,2,4-trimethylpentane. A temperature of 150-200° was required for substantial reaction and the presence of a small amount of hydrogen chloride was necessary. Compounds of higher and lower boiling range were formed in all cases and a general reaction termed autodestructive alkylation was postulated.

In 1898 Friedel and Gorgeu [4] had observed that, upon heating normal hexane with aluminum chloride on a water-bath, there was formed a considerable quantity of butane and pentane, and that propane and high-boiling products were also formed in small amounts.

On the other hand, it has also been reported that no reaction occurs between hexane and aluminum chloride at room temperature or at 55°, whereas isohexane at room temperature reacts with aluminum chloride to give products of a nature similar to those reported by Friedel and Gorgeu for hexane. Neither methane or ethane has been reported as a product of these reactions.[5]

Normal heptane, on treatment with aluminum chloride, gives rise to a greater variety of products caused by more complex molecular changes involving isomerization, condensation and cyclization. The presence of a small amount of water has an accelerating influence on the reaction. Products of these reactions ranged from propane to cycloparaffins to $C_{14}H_{26}$.[6]

In a study [3] of this reaction in the presence of a small amount of water little reaction was observed at 20-25°; at 97-99°, however, a considerable amount of gaseous paraffin was evolved and unsaturated oils were formed.

[1] J. Jurkiewicz and K. Kling, *Przemysl Chem.*, 13, 481-492 (1929); *C. A.*, 24, 1838.
[2] C. Krauch, *Oil Gas J.*, 27 (39), 156-160 (1929); *C. A.*, 23, 2284.
[3] V. N. Ipatieff and A. V. Grosse, *Ind. Eng. Chem.*, 28, 461-464 (1936).
[4] C. Friedel and A. Gorgeu, *Compt. rend.*, 127, 590-594 (1898); *J. Chem. Soc. Abs.*, 76 (1), 181 (99).
[5] V. Schneider, Thesis, "Thermal Syntheses of Aromatic Hydrocarbons," Mass. Inst. of Technology (1931).
[6] C. D. Nenitzescu and A. Dragan, *Ber.*, 66, 1892-1900 (1933).

A detailed analysis of the products formed on heating *n*-heptane with aluminum chloride at 96° has been made by Calingaert and Beatty.[7] It was found that 64.6 per cent of the heptane was converted to pentane and lower-boiling products and that 24.4 per cent went to polymers. The following hydrocarbons were identified: pentane, 2-methylpentane, 3-methylpentane, hexane, 2,4-dimethylpentane, 2,2,3-trimethylbutane, 3,3-dimethylpentane, 2-methylhexane and 3-methylhexane. There was no indication of the formation of naphthenes.[8]

Long-chain aliphatic hydrocarbons from octane to hexadecane give rise to the formation of *n*-butane when decomposed in the presence of aluminum chloride. Grignard and Stratford[9] observed from a study of the catalytic decomposition of octane, diisobutyl, decane, diisoamyl and heptadecane that butane was invariably split off. With chains of ten or more carbon atoms butane was split off from both ends of the molecule The unsaturated residues from those reactions were polymerized.

Cox[10] concluded from the decomposition of nonane by aluminum chloride at 110-120° that the pentene residue resulting from cleavage of nonane into butane was converted into cyclopentane, since the C_5H_{10} obtained was unaffected by aluminum chloride. Grignard and Stratford[9] also postulated cyclization of unsaturates in the decomposition of diisoamyl to large quantities of butane and small amounts of material which were thought to be cyclobutane and cyclopentane.

Hexadecane, when cracked in the liquid phase with aluminum chloride splits into approximately three molecules of butane and an asphaltic residue. It is significant in this work that it was observed that in the absence of a catalyst the carbon chain was likely to break at any point.[11]

The decomposition of octadecane by aluminum chloride begins at about 110° and the percentage of gaseous products increases as the reaction temperature is raised to 275°. Saturated hydrocarbons with a boiling range of 20-175°, equivalent to 60 per cent of the total reaction products, were obtained.[12] In a similar manner hexatriacontane, $C_{36}H_{74}$, began to decompose at 175°; as the temperature was increased to 315° there was considerable coke formation and a correspondingly decreased yield of liquid products.[12]

Decomposition of Naphthenic Hydrocarbons

In view of the fact that naphthenic or cycloparaffin hydrocarbons are present in petroleum and are reactants in catalytic cracking with aluminum chloride, a brief reference to the nature of the products of such reactions is important.

[7] G. Calingaert and H. A. Beatty, *J. Am. Chem Soc.*, **58**, 51-54 (1936).
[8] G Calingaert and D. T. Flood, *J Am. Chem Soc*, **57**, 956 (1935)
[9] V. Grignard and R. Stratford, *Compt. rend.*, **178**, 2149-2152 (1924) R. Stratford, *Matières grasses*, **17**, 7047-7048, 7086-7087, 7114-7116, 7294-7297, 7321-7323, 7376-7377 (1925); **18**, 7491-7497 7517-7518, 7597-7599 (1926); *C. A.*, **20**, 3230. R Stratford, *Ann. Combustible liquides*, **4**, 83-108 317-359 (1929); *C. A.*, **23**, 5564.
[10] M. V. Cox, *Bull. soc. chim.*, **37**, 1549-1553 (1925); *C. A.*, **20**, 899.
[11] H. Gault and R. Sigwalt, *Ann. office nat. comb. liquides*, **2**, 309-323, 543-584 (1927); *C. A*, **22**, 879.
[12] K. H. Bauer and V. Toma, *Ber.*, **67**, 1135-1138 (1934).

Cyclohexane, heated with aluminum chloride at 70°, polymerizes to form polycyclohexyl compounds, although this reaction does not occur at 40°. In the presence of hydrogen chloride reaction takes place even at −78° with the formation of chloropolycyclohexyl products.[13]

The isomerization of cyclohexane to methylcyclopentane was observed by Aschan,[14] but the degree to which this reaction will occur appears to be a function of the presence or absence of water. Thus Nenitzescu and Cantuniari [15] were unable to detect methylcyclopentane when cyclohexane was refluxed with anhydrous aluminum chloride; but heating with 40 per cent aluminum chloride and 1 per cent water gave a 20 per cent conversion to the isomeric methylcyclopentane. This appeared to be an equilibrium value since prolonged heating did not change the concentration; but removing methylcyclopentane from the reaction and reheating the unchanged cyclohexane and aluminum chloride again formed a mixture with 20 per cent methylcyclopentane.

It has also been reported that by heating cyclohexane with aluminum chloride there is formed not only methylcyclopentane but also a small amount of another isomer, dimethylcyclobutane.[16]

Ipatieff and Komarewsky [17] heated cyclohexane in a closed autoclave with aluminum chloride and dry hydrogen chloride at 150° for 24 hours and noted the production of methylcyclopentane, *m*-dimethylcyclohexane, bicyclohexyl, and dimethylbicyclopentyl ($C_{12}H_{22}$), together with a small amount of isobutane. Benzene under the same conditions formed ethylbenzene and biphenyl. The interpretation of these results involves destructive hydrogenation of benzene with the formation of ethylene, which in turn alkylates unchanged benzene. This process was termed "destructive alkylation." When it is applied to the reaction of cyclohexane, the derivatives of the products seem to be (1) methylcyclopentane by isomerization, (2) bicyclohexyl and dimethylbicyclopentyl by dehydrogenation of cyclohexane and methylcyclopentane, and (3) *m*-dimethylcyclohexane by destructive alkylation.

The most extensive study of the thermal decomposition of cycloparaffins by aluminum chloride is that of Grignard and Stratford.[18]

By cracking the reactants at 120-150° in the presence of 20-30 per cent by weight of aluminum chloride the following observations were made:

(1) Cyclohexane and methylcyclohexane were unchanged.
(2) *Ortho* and *para*-dimethylcyclohexanes were isomerized to the *meta*-derivative.
(3) Derivatives with a side chain of C_2 or C_3 are cracked to a slight degree (1-5 per cent) with the formation of corresponding aliphatic radicals and cyclohexene which polymerize in the presence of aluminum chloride. The side chains give rise to as many methyl groups as it has carbon atoms and these fix on the nucleus in *m*-position to each other.

[13] H. I. Waterman, J. J. Leendertse, and A. C. Ter Pooten, *Rec. trav. chim.*, **54**, 245-248 (1935); *Brit. Chem. Abs.*-A, 480 (1935).
[14] O. Aschan, *Ann.*, **324**, 1-39 (1902).
[15] C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, **66**, 1097-1100 (1933).
[16] N. D. Zelinsky and M. B. Turowa-Pollak, *Ber.*, **65**, 1171-1174, 1299-1301 (1932).
[17] V. N. Ipatieff and V. I. Komarewsky, *J. Am. Chem. Soc.*, **56**, 1926-1928 (1934).
[18] V. Grignard and R. Stratford, *loc. cit.* R. Stratford, *loc. cit.*; see also A. W. Nash and J. Mason, *Ind. Eng. Chem.*, **26**, 45-50 (1934).

(4) *m*-Diethylcyclohexane forms mainly tetramethylcyclohexane, but if the ethyl radicals are cracked off they form butane.

(5) Butylcyclohexanes are cracked more markedly (13-15 per cent). The normal and secondary compounds form *n*-butane, and the tertiary derivatives yield a mixture of *n*-butane and isobutane. The principal product is a mixture of tetramethylcyclohexanes.

(6) Amylcyclohexane is 70 per cent cracked, and isoamylcyclohexane is 42 per cent cracked to yield butane. (This indicates rupture of the side chain between the first and second carbon atoms from the ring.) Methylcyclohexane is formed in each case. Isomerisation, as before, forms tetramethyl- and pentamethylcyclohexanes.

Thus, substituted cyclohexanes undergo a double transformation: a cracking which increases in degree with the length of the side chain and an isomerization which leads only to polymethylcyclohexanes.

Cracking of heptanaphthenes from Baku petroleum at 100-140° in sealed tubes gave rise to isobutane and a carbon residue as the main products. The mechanism of this reaction has been proposed as follows [19]:

$$\text{heptanaphthene} \longrightarrow \text{cyclobutane} + H_2 \longrightarrow \text{bicyclobutane} + 2H_2$$
$$\longrightarrow \text{methylcyclopropane} + H_2 \longrightarrow \text{isobutane}$$

Decomposition of Other Hydrocarbons

Petroleum is an extremely complex mixture of hydrocarbons most of which are saturated compounds; however, when cracking takes place aromatic and unsaturated hydrocarbons are produced. The action of aluminum chloride on these latter hydrocarbons has been reviewed in Chapters 16 and 18, respectively, but the type of reactions possible should be kept in mind when considering the cracking processes.

Generally speaking, aromatic and polynuclear hydrocarbons react in the presence of aluminum chloride to form both simpler and more complex derivatives. For example, ethylbenzene forms benzene and diethylbenzene, and naphthalene heated under pressure with aluminum chloride forms some dihydronaphthalene by hydrogenation of one part of the naphthalene at the expense of the other.[20]

In an analogous manner hydroaromatic compounds such as decalin give products ranging from benzene to high-boiling compounds with condensed nuclei.[21]

Olefins will polymerize to higher olefins in the presence of aluminum chloride, and these products may isomerize to the corresponding cycloparaffins. The higher olefins may also split off lower paraffin molecules with the simultaneous formation of hydrocarbons of lower hydrogen content.[22]

The fact that the products obtained by cracking petroleum with aluminum chloride are usually low in olefins has also been attributed to the

[19] N. D. Zelinskii and V. A. Smirnov, *Brennstoff-Chem.*, **6**, 249-255 (1925), C. A., 19, 3476. C. Friedel and A. Gorgeu, *Compt. rend.*, **127**, 590-594 (1898); *J. Chem. Soc. Abs.*, **76** (I), 181 (1899).
[20] A. W. Nash and J. Mason, *Ind. Eng. Chem.*, **26**, 45-50 (1934).
[21] G. Schroeter, *Brennstoff-Chem.*, **1**, 99 (1920).
[22] H. M. Stanley, *J. Soc. Chem. Ind.*, **49**, 349-354T (1930). A. W. Nash, H. M. Stanley, and A. R. Bowen, *J. Inst. Petroleum Tech.*, **16**, 890-909 (1930).

observation that aluminum chloride combines with such unsaturates, holding them back from the distillate.[23]

As a final complicating factor it should be noted that aluminum chloride also acts as a catalyst for alkylation reactions. Under certain conditions, paraffin, naphthene, aromatic and olefin hydrocarbons will react among themselves to form a wide range of new products.[24] These reactions are discussed in more detail in Chapter 17.

Cracking of Petroleum

In 1878, Friedel and Crafts communicated to Abel [25] a description of the first aluminum chloride cracking process, and there was patented a method wherein hydrocarbons heated at 100-160° in the presence of aluminum chloride were converted to lighter hydrocarbons. Naphthalene produced benzene, toluene, and other products; low-grade petroleum gave both light and heavy oils with simultaneous removal of sulfur. Heusler [26] made similar observations, but was unable to obtain desulfurization. Gustavson [27] noted that aluminum bromide reacted in an analogous manner.

Despite the interesting implications of this pioneer work, the study was dropped for many years. Anhydrous aluminum chloride was a costly reagent and could not be used in commercial production of relatively low-priced commodities such as gasoline. The tremendous possibilities of cracking petroleum in the presence of aluminum chloride were thus held in abeyance pending the development of a cheap method of production.

The successful solution of this problem by A. M. McAfee [28,29,30] of the Gulf Refining Co. was an outstanding achievement and immediately gave rise to a great many patents covering a variety of methods of cracking petroleum.

The McAfee process for the production of gasoline from petroleum has been described in detail in many papers and patents; but reference should be made to the original literature for exact methods of operation.[31]

Briefly, this process consists of distilling crude oil to remove any water and straight-run gasoline. From 3-10 per cent of anhydrous aluminum chloride is then added to the residue and heated to 500-550°F. for 24 hours while being thoroughly agitated. Low-boiling hydrocarbons formed

[23] W. W. Henderson and W. C. Gangloff, *J. Am. Chem. Soc.*, 38, 1382-1384 (1916).
[24] V. N. Ipatieff and A. V. Grosse, *J. Am. Chem. Soc.*, 57, 1616-1621 (1935).
[25] Brit. P. 4,769 (1878) to C. D. Abel.
[26] F. Heusler, *Z. angew. Chem.*, 9, 318-321 (1896); German P. 83,404 (1894) to F. Heusler; *C. Z.*, 1895, II, 1142.
[27] G. Gustavson, *Ber.*, 14, 2619-2623 (1881); *J. Russ. Phys-Chem. Soc.*, 13, 149 (1880); *C. Z.*, 1881, 353.
[28] A. M. McAfee, *Refiner*, 8 (8), 27 (1928).
[29] U. S. P. 1,578,052 (1926) to A. M. McAfee, *C. A.*, 20, 1695.
[30] A. M. McAfee, *Ind. Eng. Chem.*, 21, 670-673 (1929).
[31] A. M. McAfee, *Ind. Eng. Chem.*, 7, 737-741 (1915); *Nat. Petroleum News*, 7, 20-25 (1915); *Chem. Met. Eng.*, 13, 592-597 (1915) and the following U. S. patents: 1,326,072-3 (1919), 1,476,091; 1,478,444 (1923), 1,501,014 (1924), 1,575,049-51; 1,601,636 (1926), 1,636,144 (1927) also Canadian P. 163,091; 163,671 (1915). See also F. W. Padgett, *Chem. Met. Eng.*, 23, 908-913 (1920). A. Mailhe, *Rev. Sci.*, 24, 325-330 (1922); C. A., 17, 1324. A. W. Nash and J. Mason, *loc. cit.* U. S. P. 1,473,316; 1,476,219 (1923), 1,577,871; 1,585,363; 1,607,966 (1926); 1,679,339 (1928) all to G. L. Prichard and H. Henderson (to Gulf Refining Co.); U. S. P. 1,976,507 (1934) to D. R. Stevens and J. R. Adams (to Gulf Refining Co.); Brit. P. 267,386 (1926) to Gulf Refining Co.

in the cracking operation are distilled off until reaction is complete. Volatilized aluminum chloride and its compounds are returned to the still. The distilled product of the reaction is a mixture of gasoline and kerosene in yields from 15-70 per cent, depending upon the type of crude used. The reaction may be continued until the still residue is reduced to a coke from which aluminum chloride may be regenerated. Alternatively, the cracking may be stopped before coking and the residual oils worked up to lubricating oils. A crude oil low in sulfur and thoroughly dried is preferred, since both sulfur and water have a tendency to reduce the activity of the aluminum chloride. Obviously this process is subject to many modifications of equipment and operating temperatures and pressures.

Another process for the catalytic cracking of petroleum with aluminum chloride has been developed by G. W. Gray and The Texas Co.[32] Substantially, this process consists of converting high-boiling hydrocarbons to low-boiling hydrocarbons by cracking, in the presence of aluminum chloride, at temperatures which are equal to the end-point of the desired product. Thus, if cracking is performed at 350°F., the over-head product will have an end-point of about 350°F.; correspondingly, operations at 550-600°F. will yield a product containing kerosene, unless a dephlegmator returns the latter to the still. It has also been noted that the addition of hydrogen chloride promotes smooth vapor evolution and tends to keep the aluminum chloride in an active condition.

The Standard Oil Company of California[33] has developed a continuous method of utilizing aluminum chloride as a cracking catalyst.

Edeleanu[34] observed that oils treated with liquid sulfur dioxide to remove unsaturated constituents may be cracked to lighter hydrocarbons by aluminum chloride. Additional aluminum chloride should be charged to the still as the boiling point of the residue increases.

Hydrocarbons soluble in liquid sulfur dioxide may be converted to a mixture of low-boiling hydrocarbons having a high content of benzene and toluene.[35] Lubricating oils may be produced by the aluminum chloride cracking of paraffin wax.[36] Oils containing unsaturated hydrocarbons may be heated with 2-10 per cent of aluminum chloride to convert these materials to saturated products before proceeding to the cracking operation.[37]

[32] Canadian P. 152,216-7 (1913), *C. A.*, **8**, 1844; Dutch P. 2,003 (1917), *C. A.*, **11**, 2731; Brit. P. 17,838-9 (1913), *J. Soc. Chem. Ind.*, **33**, 1014 (1914); U. S. P. 1,193,540-1 (1916), *C. A.*, **10**, 2402, all to G. W. Gray. U. S. P. 1,658,077 (1928) to R. J. Dearborne (to Texas Co.); U. S. P. 1,726,280 (1929) to G. D. White (to Texas Co.); U. S. P. 1,825,270 (1931) to V. N. Jenkins and C. P. Wilson, Jr. (to Texas Co.); U. S. P. 1,801,421; 1,825,294 (1931) to E. R. Walcott (to Texas Co.); U. S. P. 1,822,629 (1931) to F. W. Hall (to Texas Co.).

[33] U. S. P. 1,795,761 (1931) to Standard Oil Co. of California; U. S. P. 1,801,627 (1931) to R. W. Hanna (to Standard Oil Co. of California); U. S. P. 1,881,901 (1932) to J. H. Osmer (to Standard Oil Co. of California).

[34] U. S. P. 1,671,517 (1928) to L. Edeleanu (to Allgemeine Ges. für chem. Ind.); Brit. P. 244,097 (1924), *C. A.*, **21**, 349; Brit. P. 271,042 (1926), *C. A.*, **22**, 1677; Brit. P. 272,433 (1926), *C. A.*, **22**, 1847; Brit. P. 278,999 (1926), *C. A.*, **22**, 2053, all to Allgemeine Ges. für chem. Ind.

[35] Brit. P. 306,437 (1927) to I. G. Farbenind., *C. A.*, **23**, 4040; Brit. P. 311,789 (1927) to J. Y. Johnson (to I. G.), *Brit. Chem. Abs.*-B, 588 (1929).

[36] Brit. P. 354,441 (1931), *Brit. Chem. Abs.*-B, 916 (1931); Brit. P. 363,823 (1932), *Brit. Chem. Abs.*-B, 250 (1932) to J. Y. Johnson (to I. G.).

[37] U. S. P. 1,770,098 (1930) to J. C. Black.

The aluminum chloride process has been subjected to many modifications. Thus the oil to be converted to low boilers may be heated in a still containing a quiescent pool of aluminum chloride separated from the bottom of the still.[38] Cracking may also be conducted by contacting aluminum chloride vapors with hydrocarbon oils.[39]

Aluminum chloride has a tendency to vaporize during the cracking operation; such volatilized material may be returned directly to the still with the reflux condensate.[40] In another process, the catalyst remaining in the residue may be vaporized and absorbed in a hydrocarbon oil to be returned to the reaction chamber.[41]

The tendency of aluminum chloride to form complexes has afforded a means of preparing special catalysts. An intermediate having the formula $Al_2Cl_6C_8H_{16}.6C_6H_6$ prepared from the reaction of aluminum chloride, ethyl chloride and benzene is recommended as a catalyst, either alone or absorbed in porous materials. This latter product is used in vapor-phase cracking.[42] A similar reaction is claimed from aluminum chloride-hydrocarbon catalysts which may be formed by mixing oil and aluminum chloride,[43] or by treating oil and metallic aluminum with hydrogen chloride and supporting the catalyst in kieselguhr.[44]

The addition of other material to the aluminum chloride catalyst has been suggested; among these added reagents are charcoal,[45] hydrous silicic acid,[46] lime,[47] and very complex mixtures of alkaline-earth halides and oxidizing agents.[48]

If hydrocarbon-chlorine mixtures are passed over alumina at elevated temperatures, aluminum chloride is formed and acts upon the hydrocarbons.[49]

Residual aluminum chloride in the still residue may be removed by water washing if the end-point of the cracking operation is controlled.[50]

The aluminum chloride used in cracking petroleum may be reactivated by adding nitrosyl chloride to the charge stock.[51]

Since the recovery of aluminum chloride from the cracking operation is of vital economic concern, much work has been done on this subject. The recovery of aluminum chloride from hydrocarbon sludges thus constitutes an important section of the chapter on preparation and manufacture of aluminum chloride.*

[38] U. S. P. 1,645,533 (1927) to R. de M. Taveau, *C. A.*, 22, 162.
[39] U. S. P. 1,381,008 (1921) to C. M. Alexander and G. H. Taber, Jr.; U. S. P. 1,647,445 (1927) to F. W. Hall.
[40] U. S. P. 1,756,018 (1930) to C. P. Dubbs (to Universal Oil Products Co.).
[41] Brit. P. 189,200 (1921), *C. A.*, 17, 2498; Brit. P. 192,106 (1921), to Hoover Co.; *C. A.*, 17, 3247.
[42] Brit. P. 7,112 (1914), *C. A.*, 9, 2452, to Continental Caoutchouc and Gutta-Percha Co.
[43] U. S. P. 1,427,626 (1922) to E. V. Owen.
[44] U. S. P. 1,[illegible] (1919) to R. Koetschau.
[45] U. S. P. 1,378,653 (1921) to P. Danckwardt, *C. A.*, 15, 1990.
[46] U. S. P. 1,570,005 (1926) to H. Reinbold and H. Reinbold, *C. A.*, 20, 817.
[47] Brit. P. 277,042 (1926) to E. Schultz, *C. A.*, 22, 2461.
[48] Brit. P. 410,741 (1934) to M. A. Marconi, *C. A.*, 28, 6294.
[49] U. S. P. 1,606,246 (1926) to H. I. Lea, *Brit. Chem. Abs.*-B, 68 (1927).
[50] U. S. P. 1,322,762 (1919) to E. B. Cobb, *C. A.*, 14, 343.
[51] U. S. P. 1,936,539 (1933) (50% to H. T. Sorg); U. S. P. 1,936,633 (1933); Canadian P. 348,960 (1935), *C. A.*, 29, 3820, all to W. Leigemann.

* See Chapter 20.

The Character of the Cracked Products

With the advent of aluminum chloride cracking process a new field of research was opened up in attempting to determine the course of the reaction and the nature of the products.

Winkler [52] noted the tendency of heavy California oils to thicken when mixed with aluminum chloride. Brooks and Humphrey [53] observed the formation of aromatic hydrocarbons in the distillate obtained by cracking various oils with aluminum chloride under pressure. The high boilers were mostly naphthenes.

Pictet and Lerczynska [54] also cracked a variety of materials and found the low boilers to consist of 35 per cent paraffins and 65 per cent cyclic compounds of the formula C_nH_{2n}. They assumed that these products were formed by splitting the naphthenes with a long side chain, present in the oil, into paraffins and cycloölefins. The latter products were hydrogenated to lower-boiling naphthenes or polymerized to asphalt-like substances.

The cracking of solar oil at 250-280° with aluminum chloride gave a 70 per cent yield of low-boiling saturated hydrocarbons, whereas cracking at 600° under 18 atmospheres' pressure gave a high yield of aromatic compounds.[55]

Kerosene, spindle oils and cylinder oils decompose in the presence of aluminum chloride at 150° with the naphthenes going to paraffins, aromatics, and residual asphaltenes.[56] The mechanism of the reaction between kerosene and aluminum chloride will depend upon the source and composition of the oil. Acyclic saturated hydrocarbons will break into light, gaseous or liquid paraffins and unsaturated derivatives which may polymerize to build up higher saturated hydrocarbons. Isomerization and cyclization is also possible with these acyclics. Aromatic hydrocarbons may decompose or may be alkylated in the presence of olefins. Unsaturated hydrocarbons may polymerize to form cyclic derivatives which in turn will decompose above 150°; or they may add to the simple aromatic hydrocarbons to give higher homologs. Naphthenes are the most resistant to reaction, but above 150° they are converted to saturated compounds, and above 370° react to form aromatic and unsaturated hydrocarbons.[57]

Cracking kerosene and gas oil containing 60 per cent aromatic, 25 per cent naphthenic and 15 per cent paraffinic hydrocarbons gave about 50 per cent of a cracked distillate containing "benzene" and "toluene" fractions equal to 10 per cent of the original material.[58]

[52] J. Winkler, *J. Franklin Inst.*, 178, 97-99 (1914).
[53] B. T. Brooks and I. W. Humphrey, *J. Am. Chem. Soc.*, 38, 393-400 (1916).
[54] A. Pictet and I. Lerczynska, *Bull. soc. chim.*, 19, 326-334 (1916), *C. A.*, 10, 3154; *Arch. sci. phys. nat.*, 44, 400-401 (1917), *C. A.*, 13, 182.
[55] A. P. Lidov, *Petroleum*, 12, 413-427 (1917), *C. A.*, 13, 3005. N. D. Zelinskii, *Techn.-Wirtschaftl. Nachr.*, 193-197 (1922), *C. A.*, 18, 1746.
[56] P. P. Borisov, M. V. Gaverdovskaya, and P. F. Epefanskii, *Neftyanoe Khozyaistvo*, 27, No. 1, 74-81 (1938), *C. A.*, 29, 4926.
[57] C. Candea, Kuhn, and C. Manughevici, 14me Congr. chim. ind., Paris, Oct., 1934, 16 pp.; *C. A.*, 29, 6410. A. F. Dobryanskii and N. I. Zelenin, *Khim. Tverdogo Topliva*, 4, 606-618 (1933); *C. A.*, 28, 6239. E. Ginsburg, *Azerbaidzhanskoe Neftyanoe Khozyaistvo*, No. 6, 65-68 (1934), *C. A.*, 28, 7492.
[58] Yu. K. Yur'ev, *Neftyanoe Khozyaistvo*, No. 2, 56-59 (1938), *C. A.*, 31, 2705. S. E. Miehlina *Sci. Rep. Moscow State Univ.*, No. 3, 247-250 (1934); *Brit. Chem. Abs.-B*, 780 (1937).

The cracking of paraffin oils in the presence of aluminum chloride gave rise to a distillate containing 24 per cent aromatic and 4 per cent unsaturated hydrocarbons.[59] Although paraffin wax is not readily decomposed by aluminum chloride, 18-23 per cent yields of gasoline may be obtained, with reaction temperature below 330°.[60] Grozny paraffin heated to 130-140° with aluminum chloride gave 55 per cent of a colorless distillate. The 25-150° fraction of this distillate contained 3 per cent aromatic and 4 per cent hydroaromatic compounds; the 150-210° fraction contained less than 1 per cent aromatic or hydroaromatic compounds.[61]

Emba crude oil cracked at atmospheric pressure with 10 per cent aluminum chloride gave 48 per cent conversion to gasoline in the 50-200° range, 15 per cent boiling at 200-300° and 18 per cent boiling above 300°.[61] Refined Gabian petroleum gave a maximum conversion to light products of 74.5 per cent at 210° with 9 per cent aluminum chloride, whereas the crude material containing sulfur and oxygenated products required 14-15 per cent aluminum chloride. A distillate to 340° required 12 per cent aluminum chloride for maximum conversion. This work included a study of the stability of the complex formed between aluminum chloride and the hydrocarbons. Since it was observed that decomposition of this complex began at 150-160°, was fairly active at 190-210° and complete at 230-240°, it was deemed preferable to carry out cracking at 240-245°.[62]

It is manifestly difficult to obtain a true insight into the mechanism of decomposition of any substance as complex as petroleum oils. Practically all types of oils will yield paraffinic, aromatic and naphthenic hydrocarbons in the cracked distillate, the ratio of the products varying with the original composition of the crude. Some conclusions, however, on the influence of aluminum chloride are worth noting[63]:

Hydrogenaton of unsaturated residue formed in the decomposition of the aluminum chloride-hydrocarbon complexes occurs fairly readily. The shortage of hydrogen to complete this process permits polymerization and carbonization which limits maximum conversion to light products to about 70 per cent. Paraffin is more stable than oils containing paraffin. A maximum of 10 per cent aluminum chloride gives the optimum conversion to useful products. If temperatures above 180-195° are employed, pressure should be used to prevent sublimation of the catalyst. The complex formed between aluminum chloride and hydrocarbons is a satisfactory catalyst and simplifies handling of the aluminum chloride; however, such materials thicken and are difficult to use in a continuous manner. Cracking of oils in the presence of aluminum chloride to obtain gasoline

[59] J. Tichy, *Paliva a Topeni* 11, 85-89, 100-102 (1929), *C. A.*, 24, 4925.
[60] H. I. Waterman and L. L. W. van Soest, *J. Inst. Petroleum Tech.*, 14, 756-760 (1928); *C. A.*, 23, 967. H. Koch and H. Steinbrink, *Brennstoff-Chem.*, 20, 147-152 (1939); *Chemical Age*, 40, 358 (May 13, 1939).
[61] N. D. Zelinskii and M. E. Mikhlin, *J. Applied Chem. (U S S R)*, 6, 16-19 (1933), *C. A.*, 27, 5176.
[62] A. Graetz, *Ann. office nat. comb. liquides*, 2, 89-91 (1927), *C. A.*, 21, 3737.
[63] Dubrov, Lavrovskii, Goldstein, Fish, and Mikhnovskaya, *Neftyanoe Khozyaistvo*, 22, 19 (1933), *C. A.*, 28, 2363.

and kerosene leaves residual oils which may be used as a source of lubricating oils.

Aluminum Chloride as a Refining Agent

The use of aluminum chloride as a refining agent for lubricants and motor fuels is based on its polymerizing and desulfurizing effect. Gum-forming constituents are removed by polymerization. The desulfurizing action of aluminum chloride at ordinary temperatures is probably due to the formation of addition compounds. At higher temperatures, however, cracking occurs; most of the mercaptan sulfur is eliminated as hydrogen sulfide, but alkyl sulfides, alkyl disulfides, and thiophene are converted to hydrogen sulfide and mercaptans.[64]

Although aluminum chloride has been most often mentioned as a refining agent for petroleum products, it has been shown to be effective in removing sulfur impurities from benzene and in the purification of such a miscellany of products as wood spirit distillates, acetylene, and tetrachloroethylene.

The extensive literature on the subject is surveyed in the following table:

Table 41—Use of Aluminum Chloride in Refining

Substance Refined	Conditions	Results	Ref
Gasoline	at 30-60° with an $AlCl_3$-olefin complex	degumming	105, 115 121
Gasoline	$AlCl_3$ or $AlCl_3$-ethylene complex; subsequent or previous treatment with silent elec discharges	degumming	51, 104 117 120
Cracked gasoline	treatment with solution of $Ca(OCl)_2$ and distillation in the presence of $AlCl_3$	refining of a sweetened oil for further improvement	
Gasoline	vapor passed up a tower down which is trickled a molten 1 1 mixture of $AlCl_3$ with $ZnCl_2$ or $CuCl_2$	refining	
Cracked gasoline	$AlCl_3$ and a "moderating agent," *e.g.*, phenol at 65-480°	refining	51
Naphthene-containing gasolines		removal of substances poisoning to dehydrogenating catalysts	108
Cracked petroleum vapors	cracking vapors led directly to vessel containing 5% $AlCl_3$	high boiling constituents separated	21
Cracking distillates	slow distillation in presence of $AlCl_3$; solvent may be used	refining	74
Cracked gasoline		degumming	75
Cracked distillate	< 1% $AlCl_3$ dissolved in ethyl ether, ethyl acetate, or *n*-propyl alcohol	degumming	32 33
Cracked petroleum oil	two-stage treatment	degumming	
Cracked distillate	$AlCl_3$ in presence of a nitrohydrocarbon; *e.g.*, nitromethane	removal of undesirable compounds without substantial removal of unsaturates	
Cracked distillate, b. 150-450°	60-130°	refining	119
Petroleum fraction containing unsaturated compounds	aluminum carbide and $AlCl_3$ at 120-150°	non-sludging oil	

[64] A. E. Wood, A. Lowy, and W. F. Faragher, *Ind. Eng. Chem.*, **16**, 1116-1120 (1924).

Table 41—*(Continued)*

Substance Refined	Conditions	Results	Ref.
"Prebenzine" (from activated C absorption process)	...	degumming	2
Cracked gasoline	0.5-3% $AlCl_3$ at 400° and 1000-2000 lb./sq. in. for 20 min.	degumming	55
Heavy cut of cracked gasoline	... ...	refining	63
Crude gasoline		degumming	116
Crude gasoline stock	toned aq. soln. $AlCl_3$, under pressure	refining	64, 65, 66
Low-boiling hydrocarbons	5% $AlCl_3$ at below 35°	deodorizing and degumming	76
Hydrocarbon oil	room temperature	medicinal oil	56
Oil	mixing chamber	refining	22
Oil	distillation in presence of $AlCl_3$, series of stills	improved oil	28
Lubricating stock and lighter oil	95°	refining	37
Liquid hydrocarbons	1-2% $AlCl_3$	refining	112
Liquid hydrocarbons	solid absorbent and $AlCl_3$	refining	78
Crude oil	260-315° for 24 hours	desulfurization and degumming as a result of cracking with $AlCl_3$	10-12
Hydrocarbon oils b.p. below 260°	$AlCl_3$ on porous mass, vapor state	refining	26
Hydrocarbon oils	filtration through heated filter bed containing $AlCl_3$	refining	26a
Lubricating stock	$AlCl_3$ and moderating agent, e.g., phenol	refining	54
Mineral oils	below 100°	degumming	101
Hydrocarbon oils	the contact mass is the solid product obtained by heating Al_2O_3 with C and Cl	.	23
Paraffin- and naphthene-base oils	primary treatment with H_2SO_4, then $AlCl_3$	removal of unsaturates	30
Mineral oils	apparatus stressed	refining	47
Hydrocarbon oils	apparatus: still with propeller-blade stirrer near its bottom and agitating devices above it	refining	31
Motor oils	description of plant	refining	9
Petroleum	hydrous silicic acid and $AlCl_3$	cracking, desulfurizing, decolorizing	27
Petroleum distillate	primary refining by SO_2, then further purification with $AlCl_3$	refining	119
Lubricant stock	90-100° for material containing 90% paraffins; 130-140° for material containing not more than 50% paraffins	refining	103
Lubricating oil	activated material prepared from petrolatum and $AlCl_3$; heating for 3 hours	improvement of viscosity index	40
Solvent extracted asphalt base oils	treatment below cracking temp.	refining	42, 43
Oils	apparatus designed to eliminate corrosion by evolved HCl	.....	46
Oils	elimination of acid vapors by blowing a mixture of steam and caustic soda solution into the vapor space	.....	35
Lubricating stock	low boiling halogenated hydrocarbon and $AlCl_3$; 65-150° for 1-2 hrs., atm. pressure	refining	57

Table 41—*(Continued)*

Substance Refined	Conditions	Results	Ref
Lubricating oil	primary treatment with H_2SO_4; then $AlCl_3$ at about 120° to remove sulfonic acids present	ash-free lubricating oil	50
Lubricating stock	10% $AlCl_3$ and 10% fuller's earth for 0.5 hour at 175°	refining	60
Lubricating oil	two-stage treatment; at 205-246°, removing sludge, and then at 144-177°	improvement of viscosity	66
Used lubricating oils	130-140°	purification and regeneration	60, 106
Lubricating oil	3-10% $AlCl_3$ at above 200° for 0.5-4.0 hours	dewaxing	58
Hydrocarbon oils	preliminary treatment with a "conditioning agent," *e.g.*, nitrobenzene	refining	111
Mineral and tar oils, b.p. 200-300°	$AlCl_3$ and finally divided metals, *e.g.*, a mixture of copper, bronze and powdered nickel, 100-200°	viscosity improvement	100
Mineral oils containing aromatic and non-aromatic hydrocarbons	acetylene and $AlCl_3$	separation of aromatic hydrocarbons	67
Mineral oil	$AlCl_3$ in a solvent comprising an ether and an alcohol; *e.g.*, a mixture of ethyl ether and propyl alcohol	degumming	34
High boiling mineral lubricating oils	150°F. for at least 24 hours	refining	73, 110
Crude asphaltic petroleum	5% $AlCl_3$ or Al+Cl	refining	18
Cracking or sludge residue	100-200° with or without addition of a little water	removal of asphaltic substances	77
Carbon monoxide hydrogenation products, b. above 250°	....	refining	109
Solvent extract of cracked products from paraffin wax, ozokerite, or ceresin, b.p. 150-450°	....	refining	107
Paraffin	65°	purification	19
Petrolatum	agitation with 10-20 wt. % of $AlCl_3$ at 80-120°; six treatments with removal of sediment after each treatment	purification	38
Aliphatic hydrocarbons of more than 10 carbon atoms	50-110° with 1-3% $AlCl_3$	removal of substances hindering oxidation	122
Benzene	1% $AlCl_3$	removal of unsaturated compounds through polymerization or, if less $AlCl_3$ is used through reaction with the benzene (alkylation)	8
Xylene	.....	Purification so that xylene may be used as solvent for catalytic reactions. One treatment with $AlCl_3$ equivalent to 12 washings with concd. H_2SO_4	17
Lignite tars	100-200°	viscous oils	114
Light oils from coal carbonisation	$AlCl_3$ and H_2SO_4	refining	102
Oils from brown coal tars	100-200°	dewaxing	79
Sulfurised oil, terpene, or terpene compound	inert solvent such as gasoline	refining	71

Table 41—*(Continued)*

Substance Refined	Conditions	Results	Ref.
Wood tar	....	improvement of inhibiting properties	70
Acetone oils, b. 125-200°, in wood spirit distillates, b. 125-195°	....	decolorizing	113
Rosin	....	decolorizing	36
Sulfur contaminated with hydrocarbons	molten sulfur	purification	30
Acetylene	10-30°	purification from unsaturated impurities	123
Tetrachloroethylene	1% $AlCl_3$ at the b.p.	purification	53
Phthalic anhydride	$AlCl_3$ stirred with molten phthalic anhydride; subsequent distillation	purification	41
	Desulfurization		
Petroleum oils	LiCl and $AlCl_3$	decolorization and desulfurization	25
Petroleum oils	0.5-4% $AlCl_3$ at 100-150°	desulfurization	44
Petroleum oils	equimolecular mixture of $AlCl_3$ and cresylic acid	desulfurization	52
Hydrocarbons	100-600°	desulfurization	72
Tar and petroleum distillates	....	incomplete removal of sulfur	5
Cracked gasoline	5-10% $AlCl_3$ for 2 hours	sulfur reduced from 1 to 0.01%	7
Kerosene	65°	decolorization, deodorization	20
Cracked petroleum distillate	acetone and $AlCl_3$	desulfurization	45
Cracked gasoline	SO_2 and $AlCl_3$, vapor phase	refining	61
Gasoline	Zn and $AlCl_3$, vapor phase	desulfurization	62
Cracked gasoline	1% by wt. of $AlCl_3$	sulfur content reduced 50%	1
Stehtamuk gasoline	1-5% $AlCl_3$	removed: allyl sulfide, *sec*-heptyl sulfide, and benzyl sulfide; *n*-heptyl sulfide, ethyl sulfide, and ethyl disulfide only slightly attacked	16
Gasoline	0.5% $AlCl_3$ at 30-40°	desulfurization; $AlCl_3$ forms liquid compounds with the S compounds	13
Pure organic S compounds dissolved in naphtha	experiments with isoamyl- and isobutyl mercaptan, alkyl- and di-alkyl sulfides, and with thiophene indicate that at ordinary temperatures desulfurization takes place through formation of addition compounds; at higher temperatures through cracking and evolution of H_2S		14
Crude xylene and cumene	.....	desulfurization	5
Benzene	repeated treatment with cold $AlCl_3$ at 35°	removal of thiophene	6
Benzene	agitation with 1-5% of $AlCl_3$ depending upon the purity of benzene treated	purification from thiophene, its homologs, and other impurities	8
Toluene	same as above	results less satisfactory than with benzene	8
Pure organic sulfur compounds in naphtha solution	.....	good desulfurizing of solutions containing isoamyl-, *n sec*-heptyl-, allyl-, phenyl-, and benzyl sulfides. Ethyl- and *n*-heptyl sulfide and ethyl disulfide little affected.	15

Table 41—*(Continued)*

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Preparation of Lubricants and Addition Agents for Lubricants by Reaction of Aromatic Compounds with Higher Alkyl Halides or Acyl Halides

The condensation of chlorinated aliphatic hydrocarbons of high molecular weight with benzene or its homologs in the presence of aluminum chloride results in products useful as lubricants. The chlorinated aliphatic hydrocarbon may be chlorinated paraffin wax containing 15-30 per cent chlorine. The lower layer of the reaction product serves as a catalyst for further condensations.[65] The upper layer can be separated from the reaction mixture by filtration through a solid reagent and subsequent treatment with ammonium hydroxide.[66] Another method[67] comprises preliminary mixing of the chlorinated hydrocarbon with the aromatic hydrocarbon in the absence of catalyst, cooling of the mixture to cause separation of solids, which are removed, and treatment of the residual liquid with aluminum chloride, if desired with the addition of a further quantity of the aromatic hydrocarbon.

[65] British P. 478,972 (1938) to Imperial Chemical Industries.
[66] British P. 485,163 to A. P. Lowes, D. E. White, and Imperial Chemical Industries.
[67] British P. 483,316 (1938) to A. P. Lowes, D. E. White, and Imperial Chemical Industries; *C. A.*, 32, 7258.

The production of synthetic lubricating oils by condensation of a chlorinated hydrocarbon wax with about 5-25 per cent its quantity of biphenyl in the presence of about 1-15 per cent its quantity of aluminum chloride at 55-60° has been claimed.[68]

Lubricants have been prepared from Kogasin by preliminary preparation of alkyl chlorides from the high molecular weight paraffins secured by hydrogenation of carbon monoxide, and subsequent condensation of the alkyl halides with aromatic hydrocarbons in presence of aluminum chloride. Viscosities and viscosity-temperature curves of the products obtained have been determined.[69]

The production of addition agents for lubricating oils by reaction of chlorinated paraffin wax with aromatic hydrocarbons in the presence of aluminum chloride was announced in 1931 by Davis.[70] Paraffin wax was chlorinated at 60-150° to a product containing 10-12 per cent chlorine, and 1 part of this material was reacted with 0.1-0.5 part of aromatic material such as benzene, naphthalene, anthracene, or aromatic gas oil The whole was mixed with an equal weight of aluminum chloride at 60-71° in the presence of kerosene as diluent, and after 24 hours the temperature was raised to 93°. The reaction mixture was allowed to settle, the oil cooled, and the unchanged paraffin removed by cold-pressing or vacuum distillation.

Products of the Friedel-Crafts condensation of the chlorinated paraffin wax with naphthalene are known to the trade as Paraflows. Addition of 0.25 to 1.5 per cent of paraflow to paraffin-base oils reduces the pour-point from around 30°F. to 0°F.[71]

The heavy, unctuous synthetic product obtained by condensing chlorinated paraffin with benzene or naphthalene has been claimed to be an effective additive to heavy lubricants for transmission and differential gears.[72] According to Suida and Poll,[73] however, paraflow cannot be used with transformer oils or with other oils used for lubrication over long periods of time since oils so treated age more easily. These investigators also report that oils from purely asphalt-base crude containing no paraffin are unaffected by addition of paraflow.

In an improved process[74] halogenated heavy aliphatic hydrocarbons are heated with an aromatic compound such as naphthalene, biphenyl, chlorinated biphenyl, fluorene, chlorinated anthracene, or coal-tar residue to a reaction temperature of about 55°, and aluminum chloride is subsequently added, the reaction temperature being kept at 54-60° for one to four hours, or until reaction is complete. The residue is extracted with

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an organic solvent, such as carbon tetrachloride or chloroform, the extract being neutralized and the solvent removed. The product thus secured is claimed to be two or three times as effective as paraflow prepared by the older method. Operating details for the process are described.

Low temperatures are used in another method.[75] Grozny paraffin (m.p. 55°) was chlorinated at 65° to a content of 13 per cent chlorine. To a solution of naphthalene in kerosene the molten chlorinated paraffin was gradually added, together with aluminum chloride, and condensation was effected in two hours at 5°. The mixture was steam-distilled, and the residue was paraflow, having a molecular weight of 900-1000.

The yield of wax modifiers obtained may be increased by condensing halogenated paraffin wax with an aromatic hydrocarbon and aluminum chloride at low temperatures, and after the initial stage is substantially complete, separating the lighter, inactive intermediate reaction products so formed from heavier active products, and recondensing the lighter products with a low molecular weight aliphatic poly-halohydrocarbon derivative.[76]

As noted elsewhere,* oily or resinous products are secured by reaction of poly-halogenated olefins or paraffins with aromatic hydrocarbons in the presence of aluminum chloride. When the reaction of a dichloro- paraffin, such as ethylene dichloride, and benzene is effected in the presence of oleic acid and the catalyst, pour-point depressors are obtained.[77]

The chlorinated aliphatic hydrocarbon may be the reaction product of high molecular weight hydroxy- compounds with a halogenating agent such as phosphorus trichloride. The hydroxy- groups of such higher alcohols as oleyl alcohol or stearylene glycol are thus replaced by halogen, and a chloroparaffin is obtained which, when condensed with cyclic or olefinic compounds, yields a substance which improves the temperature-viscosity curve of lubricating oils or greases.[78]

As the aromatic component, a previously polymerized, unsaturated isocyclic compound containing unsaturation in the nucleus may be used. Friedel-Crafts condensation of chlorinated paraffin wax with polymerized dihydronaphthalene, for example, gives a product which improves pour-point characteristics of lubricating oils.[79]

Chlorinated hydrocarbons may be used as solvents for the reaction. Thus, wax-modifying agents are obtained by Friedel-Crafts condensation at about 90° of halogenated paraffins with aromatic compounds containing not more than three substituents and/or condensed rings in the presence of a solvent which is substantially inert under the reaction conditions, for example, trichloroethylene, tetrachloroethylene, tetra-, penta-, or hexachloroethane, or a polychlorobenzene.[80]

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[79] British P. 510,952 (1939) to Standard Oil Development Co.; *Brit. Chem. Abs.*-B, 1096 (1939).
[80] British P. 511,207 (1939) to Standard Oil Development Co.; *Brit. Chem. Abs.*-B, 1098 (1939).

According to Ramayya and Khaiman,[81] the paraflow secured by reacting a chlorinated wax containing 13-16 per cent chlorine with naphthalene is a dialkylated naphthalene in which each of the two side chains consists of at least 25 carbon atoms. The chlorine atoms of the dichlorinated paraffin obtained in the halogenation step participate in the condensation reaction with naphthalene. The use of a dichlorinated paraffin wax for the production of a pour-point depressor was later specified by MacLaren,[82] who secured dichlorinated wax, containing about 14 per cent chlorine, by solvent extraction of chlorinated paraffin wax with petroleum naphtha, isopropyl ether, sulfur dioxide, or liquid propane. Frolich [83] prepares a pour-point depressor by stepwise alkylation of an aromatic hydrocarbon first with a chlorinated wax containing more than 12-15 per cent chlorine, isolating the reaction product, and alkylating it with a chlorinated wax containing not more than 10 per cent chlorine—probably only a mono-chlorinated wax.

Various methods of isolating the alkylated product have been devised. The kerosene and the uncondensed paraffin can be eliminated by distillation in vacuum or with steam.[84] The pour-point depressor may be extracted with an organic solvent such as carbon tetrachloride or chloroform, the extract neutralized, the solvent removed, and the impurities removed by washing.[85] The crude product may be freed from the catalyst by treating at 280-300° with ammonia, or an anhydrous halide, sulfate, or phosphate of a metal of group II, and separating the granular compound formed.[86] Another way of freeing the lower layer from the catalyst consists in warming it with dilute hydrochloric acid and then heating at 300-400° until a homogeneous melt is obtained. The solid matter is subsequently removed by dissolving in a solvent, for example, benzene or toluene, filtering, and distilling off the solvent.[87]

Purification of the crude wax resin obtained by Friedel-Crafts reaction of chlorinated wax with an aromatic hydrocarbon may be effected by dissolving it in liquefied propane, and heating the solution to about 43-49°, while maintaining the mixture under a pressure sufficient to keep the propane in liquid form, and separating the purified synthetic wax resins insoluble in propane at this temperature.[88] Amyl or butyl alcohol may also be used as the extracting agent.[89] The wax resin may also be purified by neutralizing the reaction products with an oil having a Saybolt universal viscosity of 100-250 seconds at 38°, heating the mixture thus formed to about 75-93°, introducing live steam into the mixture

[81] H. S. Ramayya and S. Khaiman, *Neftyanoe Khozyaistvo*, **26**, No. 12, 37-44 (1934); *C. A.*, **29**, 4028.

[82] U. S. P. 2,080,307 (1936) to Standard Oil Co. of Indiana; *C. A.*, **30**, 2365; *Brit. Chem. Abs.*-B, 211 (1937).

[83] U. S. P. 2,015,748 (1935) to P. K. Frolich (to Standard Oil Development Co.); *Brit. Chem. Abs.*-B, 1132 (1936).

[84] O. O. Heiman, *Azerbaidzhanskoe Neftyanoe Khoz.*, No. 3, 66-71 (1938); *Chimie et industrie*, **40**, 1067; *C. A.*, **33**, 2691.

[85] U. S. P. 1,962,917 (1934) to F. H. Macilaren (to Standard Oil Co. of Indiana); *C. A.*, **28**, 5226.

[86] British P. 473,334 (1936) to A. W. Nash, T. G. Hunter, W. R. Wiggins, A. P. Lowes, and Imperial Chemical Industries; *Brit. Chem. Abs.*-B, 1313 (1937).

[87] British P. 477,928 (1936) to C. Ockrent, D. W. F. Hardie, and Imperial Chemical Industries, *Brit. Chem. Abs.*-B, 1130 (1938).

[88] U. S. P. 2,113,179 (1938) to W. B. Kay (to Standard Oil Co.).

[89] U. S. P. 2,045,896 (1936) to R. G. Sloane (to Standard Oil Development Co.).

until it is heated to about 99-105°, then permitting settling, and separating the purified wax resin from undesirable reaction products.[90] Aluminum chloride has been claimed to be an effective refining agent for this purpose. The alkylation product is stirred at 80° with water, freed from diluent by distillation, dissolved in heavy gasoline, refined by treatment at 50° with 2 per cent of aluminum chloride, filtered from solid hydrocarbons, and freed from gasoline by distillation.[91]

Various after-treatments of paraflow have been claimed to improve its efficiency. Among these may be cited its halogenation, to the extent of from 5 to 20 per cent,[92] resinification with trioxymethylene,[93] or admixture with montan wax or an ester of montanic alcohol and montanic acid.[94] An improved product may also be obtained by first condensing chlorinated waxy hydrocarbons with a chlorinated cyclic hydrocarbon by means of aluminum chloride, removing remaining halogen, and producing a further condensation by means of a condensing reagent like sodium.[95] Acylation has been suggested. Thus, chlorinated paraffin wax is condensed with an aromatic hydrocarbon in the presence of aluminum chloride, and the product is subsequently recondensed with 0.25-1.0 mole of an acyl halide per 250 g of the original condensation product.[96]

The translucence, viscosity, and pour-point depressing effectiveness of long-chain alkyl naphthalenes may be improved by subjecting them to relatively mild treatment with silent electric discharge.[97]

The condensation of halogenated higher paraffins with polynuclear aromatic hydrocarbons in the presence of aluminum chloride and sodium chloride or cupric chloride leads to the production of substances which impart to lubricating oils a green fluorescence stable to light and oxidation. Preferably, at least 25 per cent of aluminum chloride and at least 20 per cent of aromatic hydrocarbon are taken, calculated on the haloparaffin used. If sodium chloride is omitted, the products are likely to impart an undesired bluish fluorescence which is unstable to light.[98]

Oily condensation products useful for imparting color and fluorescence to lubricating oils may be also secured by condensing by means of aluminum chloride an aromatic hydrocarbon such as benzene, toluene, or naphthalene with a chlorinated long-chain aliphatic hydrocarbon containing about 40 per cent chlorine, separating the lower of the two layers formed, removing the catalyst from it by heating with dilute hydrochloric acid, and then heating at 300-400° until a homogeneous melt is obtained.[99]

[90] U. S. P. 2,057,104 (1936) to Standard Oil Co. of Indiana; *C. A.*, **30**, 8600.
[91] British P. 415,065 (1934) to I. G. Farbenindustrie; *C. A.*, **29**, 922.
[92] U. S. P. 2,172,382 (1939) to A. Henriksen and B. H. Lincoln (to the Lubri-Zol Development Corp.).
[93] U. S. P. 2,052,002 (1936) to O. M. Reiff (to Socony-Vacuum Oil Co.).
[94] U. S. P. 2,081,518 (1937) to M. L. Wade (to Union Oil Co.); *Brit. Chem. Abs.*-B, 1095 (1939).
[95] U. S. P. 2,049,058 (1936) to A. H. Gleason (to Standard Oil Development Co.).
[96] British P. 509,550 (1939) to Standard Oil Development Co.; *Brit. Chem. Abs.*-B, 1020 (1939).
[97] British P. 479,479 (1938) to Standard Oil Development Co., *C. A.*, **32**, 5199; Can. P. 377,840 (1938) to J. A. Tilton and R. W. Richardson (to Standard Oil Development Co.); *C. A.*, **33**, 2323.
[98] German P. 603,269 (1934) to H. Rabe (to I. G.), *C. A.*, **29**, 596; U. S. P. 2,062,472 (1936) to I. G., *C. A.*, **30**, 1989.
[99] British P. 477,923 (1935) to C. Ockrent, D. W. F. Hardie, and Imperial Chemical Industries; *C. A.*, **32**, 4776.

Small amounts of paraflow inhibit excessive growth of crystals.[100] When liquid polishing wax is treated with a few per cent of paraflow, undesirable crystallization of constituents in the polishing composition is prevented.[101] Paraflow is used as a crystallization regulator in dewaxing lubricating oils.[102]

In a thorough study dealing with the condensation of chlorinated paraffin wax with aromatic hydrocarbons in the presence of aluminum chloride or of metallic aluminum as catalyst, it was found that metallic aluminum gives better yields than does aluminum chloride and that the oil obtained with the former is of a better quality.[103]

Uses of Phenols.—Phenol or its derivatives condenses with chlorinated paraffin wax in the presence of aluminum chloride to yield a product which finds use as a pour point depressor for lubricating oils.[104] Various after-treatments of the pour-point depressor thus secured have been suggested. An improved product is secured by subsequent condensation with a resinifying agent like hexamethylenetetramine,[105] or esterified with a carboxylic acid derivative, for example, with phthaloyl chloride.[106] Conversely, the phenol may first be condensed with a resinifying agent such as an aldehyde, and subsequently reacted with the chlorowax and aluminum chloride.[107]

Acylation.—Products useful as pour-point depressors for lubricating oils may be obtained by reacting higher acyl halides with coal-tar fractions, preferably those boiling above 200°, in the presence of aluminum chloride. The addition of 0.1 to 1 per cent of the reaction product of stearoyl chloride and anthracene to lubricating oils improves their viscosity and reduces the pour-point.[108]

Auto-condensation of Chlorinated Higher Paraffins to Yield Lubricants or Pour-point Depressors

When chlorinated paraffins are treated with aluminum chloride in the absence of an aromatic hydrocarbon, condensation occurs which results in production of substances which also serve for improving the pour properties of lubricating oils. Since either high molecular weight olefins or chlorinated paraffins may be used, it can be assumed that the aluminum chloride-catalyzed condensation of chloroparaffins for production of pour-

[100] G. H. B. Davis, *National Petroleum News*, **24** (52), 32, 34 (1932); *C. A.*, **27**, 1494.
[101] U. S. P. 2,010,297 (1935) to M. T. Flaxman (to Union Oil Co.).
[102] U. S. P. 1,998,747 (1935) to C. E. Adams (to Standard Oil Co. of Indiana); U. S. P. 2,007,127 (1937) to R. E. Manley (to The Texas Co.), *C. A.*, **32**, 346; U. S. P. 2,081,519 to M. L. Wade (to Union Oil Co. of California), *C. A.*, **31**, 5152; U. S. P. 1,998,848 (1935) to J. A. Anderson (to Standard Oil Co. of Indiana), *C. A.*, **29**, 3822; U. S. P. 2,003,674 (1935) to A. Berne-Allen (to Standard Oil Development Co.), *Brit Chem. Abs.*-**B**, 779 (1936); French P. 533,787 (1938) to Standard Oil Development Co., *C. A.*, **33**, 3580.
[103] W. R. Wiggins, T. G. Hunter, and A. W. Nash, *J. Inst. Petroleum*, **26**, 129-145 (1940).
[104] Brit. P. 474,240 (1937) to Socony-Vacuum Oil Co., *C. A.*, **32**, 3602; French P. 805,693 (1937) to Socony-Vacuum Oil Co., *C. Z.*, 1937 II, 1117.
[105] U. S. P. 2,062,876 (1936) to Socony-Vacuum Oil Co., *C. A.*, **31**, 847.
[106] British P. 491,328 (1937) to O. M. Reiff and D. E. Badertscher (to Socony-Vacuum Oil Co.), *Brit. Chem. Abs.*-**B**, 1368 (1938); Can. P. 375,607 (1938) to O. M. Reiff and D. E. Badertscher (to Socony-Vacuum Oil Co.), *C. A.*, **32**, 7717.
[107] U. S. P. 2,061,008 (1936) to Socony-Vacuum Oil Co., *C. A.*, **31**, 848.
[108] U. S. P. 2,039,545 (1936), Brit. P. 473,846 (1937), Can. P. 366,296 (1937), all to A. W. Ralston, C. W. Christensen, and S. T. Bauer, (to Armour and Co.); *Brit. Chem. Abs.*-**B**, 208 (1937); *C. A.*, **31**, 5154.

point depressors proceeds through intermediate dehydrohalogenation, and subsequent polymerization of the resulting olefins.[109]

In one method, condensation is brought about by first chlorinating paraffin wax and then condensing it in a kerosene medium by means of aluminum chloride. The temperature of chlorination is preferably 94 to 177°, and that of condensation is preferably about 21 to 66°. Condensation takes place within about 24 hours.[110] An improved process specifies that the condensation be stopped before its normal conclusion; it is claimed that valuable inhibiting powers are thus preserved.[109]

Uniform products are secured if, before condensation, the halogenated paraffins are separated by fractional distillation, or deposition by cooling. Thus, when chlorinated paraffins are separated by cooling in presence of a solvent like acetone, the monochloro- product is separated first, then the dichloro- product, and subsequently the trichloro- product.[111]

The same type of condensation occurs when aliphatic solid or semi-solid hydrocarbons having exchangeable substituents other than chlorine are treated with aluminum chloride.[112] Thus, condensation of high molecular weight paraffin hydrocarbons may be effected by submitting the hydrocarbons to the action of chlorine, oxygen, or sulfur and then treating with aluminum chloride.[113]

Although the material ordinarily used for the preparation of pour-point depressors is paraffin wax, alkyl chlorides obtained by treating higher alcohols having at least 12 carbon atoms with a halogenating agent, such as thionyl chloride, have been used for this purpose.[114]

A recent modification comprises halogenating paraffin wax with a halogenating agent such as chlorine until it contains 10-60 per cent halogen while relatively unstable halogenated compounds are formed, and then condensing the reaction mixture with aluminum chloride just sufficiently to convert the unstable constituents into stable constituents, without substantially modifying the relatively stable constituents. The products thus obtained are high-pressure lubricants.[115]

Antioxidants for lubricating oils are secured by reacting chlorinated paraffin wax and oleic acid with aluminum chloride, reacting the product of this reaction with lime, and recovering the antioxidant product by distillation from the resulting mixture.[116]

Oily condensation products have been secured by condensing chlorinated aliphatic hydrocarbons of high molecular weight in the presence of aluminum chloride, then treating the reaction product with the hydroxide

[109] U. S. P. 2,057,682 (1937) to G. H. B. Davis and C. C. Swope (to Standard Oil Development Co.); Dutch P. 68,597 (1932) to Standard Oil Development Co.; British P. 396,147 (1933) to G. M. Maverick (to Standard Oil Development Co.); *C. A.*, 28, 632.

[110] British P. 402,858 (1933); German P. 582,853 (1933) to Standard Oil Development Co.

[111] British P. 417,689 (1934) to I. G. Farbenindustrie, *C. A.*, 29, 1242; French P. 766,516 (1934) to I. G. Farbenindustrie, *C. Z.*, 1936 I, 1160

[112] British P. 349,071 (1930) to I. G. Farbenindustrie, *C. A.*, 26, 2048.

[113] French P. 743,521 (1933) to I. G. Farbenindustrie, *C. A.*, 27, 3812.

[114] U. S. P. 2,147,315 (1939) to M. Pier and F. Christmann (to I. G.), *C. A.*, 33, 4016.

[115] U. S. P. 2,110,856 (1938) to C. F. Prutton (to Lubri-Zol Development Corp), *C. A.*, 32, 6052.

[116] U. S. P. 2,101,241 (1937) to J. Cole (to Sinclair Refining Co.).

or anhydrous sulfate or phosphate of iron, chromium or aluminum at 250-300°, and separating the oil by decantation or filtration.[117]

The condensation products secured by treatment of chlorinated wax with aluminum chloride may be used in dewaxing lubricating oils. It serves to modify the wax crystal structure upon chilling a wax-bearing oil.[118]

[117] British P. 498,715 (1938) to A. P. Lowes (to Imperial Chemical Industries).
[118] U. S. P. 2,097,127 (1937) to R. E. Manley (to The Texas Co.), *C. A.*, 32, 340

Chapter 20

Preparation and Manufacture of Anhydrous Aluminum Chloride

In the laboratory, aluminum chloride is most readily secured by passage of chlorine or hydrogen chloride over heated aluminum filings. Due to its importance in the petroleum industry as a cracking, refining, and polymerizing agent, much work has been done on the commercial manufacture of aluminum chloride from bauxite or other aluminiferous ores. The process developed by the Gulf Refining Company at Port Arthur, Texas, using bauxite and chlorine, has made available technical anhydrous aluminum chloride at eight and a half cents per pound, including drum costs.[1] In 1938, the total production of crystal and anhydrous aluminum chloride in the United States was 6,240 short tons.[2]

Besides aluminum and aluminiferous ores, various compounds of aluminum, such as aluminum sulfate, aluminum phosphate, aluminum nitride, or aluminum carbide, have been used for the preparation of aluminum chloride. Chlorination has been effected with chlorine, hydrogen chloride, metal chlorides, or other chlorine compounds. The discussion that follows has, therefore, been subdivided according to the following scheme:

- Metallic aluminum
  - Reaction with chlorine
  - Reaction with hydrogen chloride
  - Reaction with other chlorides
- Alumina or aluminiferous ores with or without a carbonaceous reducing agent
  - Reaction with chlorine
  - Reaction with hydrogen chloride
  - Reaction with metallic chlorides
  - Reaction with sulfur chlorides or a mixture of sulfur and chlorine
  - Reaction with carbon monoxide and chlorine or with phosgene
  - Reaction with miscellaneous chlorides
    - Carbon tetrachloride
    - Chlorides of phosphorus
    - Ammonium chloride
    - Silicon tetrachloride
- Aluminum compounds
  - Reactions with many of the above-mentioned chlorinating agents
- Preparation of anhydrous aluminum chloride by dehydration of $AlCl_3 . 6H_2O$
- Preparation of anhydrous aluminum chloride by recovery from sludges resulting from the treatment of petroleum with aluminum chloride
- Purification of aluminum chloride

[1] Quotation from Gulf Refining Company, August 5, 1941.
[2] Bureau of Mines Yearbook, p. 638, Government Printing Office, Washington, 1939. Four producers of anhydrous aluminum chloride are noted.

A number of good reviews dealing with the preparation of anhydrous aluminum chloride are available.[3]

Especially valuable is Ralston's[4] in which information is given concerning eleven processes, and comment is made on the cost of raw material and economic feasibility.

Preparation of Aluminum Chloride from Metallic Aluminum

Reaction with Chlorine.—In 1887, Wohler[5] reported that when aluminum filings are heated to glowing in gaseous chlorine, combustion occurs with formation of sublimed aluminum chloride. The preparation was later substantiated by Weber[6] and improved by Gustavson,[7] who gently warmed aluminum foil, contained in a hard glass tube, in a current of chlorine. The aluminum chloride distilled over into a receiver.

An efficient laboratory method for preparation of aluminum chloride is described by Gomberg.[8] About 50 g of well washed and dried aluminum filings were placed in an iron receiver and connected with a chlorine generator. The part of the tube adjacent to the receiver was gently heated, and a stream of chlorine was rapidly introduced. The gas attacked the cold part of the metal immediately. Since the heat of reaction was very great, 8 to 10 cm of the metal became glowing. Reaction was completed in seventy-five to ninety minutes. The yield of aluminum chloride was 190-200 g, or about 80 per cent of theoretical.

Pure anhydrous aluminum chloride, for use in electrolysis, has been prepared by chlorination of aluminum filings, containing 99.997 per cent aluminum, with pure chlorine.[9]

According to Ralston,[10] the heat of the reaction melts down the finely divided aluminum into globules, which present a minimum of surface to the reaction. A film of aluminum oxide which forms on the aluminum particles or on a bath of molten aluminum chloride also interferes with efficient absorption of chlorine. It is, therefore, necessary to force the gas through the protective film. This idea is carried out in a patent to Brooks,[11] who described the preparation of aluminum chloride by passing a stream of chlorine through molten aluminum under pressure, or with sufficient rapidity to keep the metal agitated. He used a graphite reaction vessel.

Anhydrous Metallic Chlorides Corporation claims the use of an externally heated reaction vessel made of fused silica. One end of the vessel

[3] M. F. Bouriot, *Ann. chim phys.*, 20, 547 (1910), *C. A.*, 4, 2917. F. Delaroniere, *Rev. prod chim.* 35, 545, 609-618, 645-648 (1932), *C. Z.*, 1933 I, 476. K. H. Klipstein, *Chem. Markets*, 25, 593-595 (1929), *C. Z.*, 1930 I, 1515. O. C. Ralston, *Chem. News*, 127, 246-248 (1923), *C. Z.*, 1924 I, 629. C. Simon, *Chim. et industrie*, 24, 1317-1324 (1930), *C. A.*, 25, 1641; Gmelin's "Handbuch der anorganischen Chemie," 8 Auflage, Aluminum, Teil B, p. 164-182, Berlin, 1934.

[4] O. C. Ralston, Bur. of Mines Tech. Paper 321, 38 pp. (1923).

[5] F. Wohler, *Pogg. Ann.*, 11, 158 (1827).

[6] R. Weber, *Pogg. Ann.*, 103, 269 (1858).

[7] G. Gustavson, *J. prakt. Chem. (2)*, 63, 110-112 (1901), *J. Chem. Soc. Abs.*, 80 (II), 816 (1901). *Bl. soc. Naturalistes Moscow*, No. 2 (1900).

[8] M. Gomberg, *Ber.*, 33, 3144-3149 (1900).

[9] J. Czochralski and J. Mikolajczyk, *Wiadomosci Inst. Metalurg. Metalos.*, 5, 58-60 (1938), *C. I.* 32, 7822.

[10] O. C. Ralston, "Anhydrous Aluminum Chloride," Bureau of Mines Tech. Paper 321 (1923).

[11] U. S. P. 1,165,065 (1915) to B. T. Brooks, *C. A.*, 10, 873; Can. P. 222,213 (1922) to B. T. Brooks, *C. A.*, 16, 4021.

is outside the heating zone and is connected with the chlorine supply; the other opens into a chamber through which aluminum chloride escapes.[12]

It has been found by Evans[13] that the rate of surface attack of aluminum by chlorine at 134-254° and 100-600 mm pressure is independent of the pressure and has an apparent energy of activation of 2000 g cal. The reaction rate does vary with the temperature as well as with the surface conditions of the aluminum.

Since oxidation of aluminum should be prevented during the process, one method for the preparation of aluminum chloride from molten aluminum and chlorine involves not only agitation, but also the addition of a carbonaceous material, such as charcoal, which acts as a reducing agent.[14]

A carbonaceous reducing agent is used in the preparation of aluminum chloride from pulverulent aluminum dross. Here the carbon reduces the alumina which surrounds the small droplets of aluminum metal present in the dross. The heat of reaction of chlorine with the metallic aluminum also serves to effect the chlorination of the alumina.[15]

The influence of impurities in aluminum upon the temperature of chlorination has been investigated by Koch,[16] who found that the temperature of volatilization of pure aluminum is reduced by impurities, especially by iron and silicon, and that at the same time the volatility of aluminum chloride is increased. The impurities also minimized the formation of a protective film over the molten metal. Warren[17] describes the preparation of aluminum chloride by chlorinating a pulverized alloy of iron and aluminum. If the alloy is mixed with sodium chloride previous to chlorination, a sublimate of aluminum sodium chloride is obtained.

Aluminum seems to be unaffected by liquid chlorine at its boiling point, but at −20°, combination occurs, with incandescence.[18] The preparation of aluminum chloride by reaction of aluminum with liquid chlorine has been patented. Thin aluminum scraps are treated with liquid chlorine in an iron autoclave which is equipped with a chilled condenser for absorbing the heat of reaction. Pressures of 1 to 5 atmospheres and temperatures of below 0°, preferably −33°, may be used.[19] A modification of the process involves maintaining a source of chlorine in constant communication with the liquid chlorine in the reaction chamber. A flow of chlorine vapors is established between the reaction chamber and a second body of liquid chlorine maintained at a higher and constant temperature.[20]

[12] Dutch P. 21,840 (1930) to Anhydrous Metallic Chlorides Corporation; *C. Z.*, 1930 II, 1267; German P. 502,676 (1925) to Anhydrous Metallic Chlorides Corporation.
[13] M. G. Evans, *Mem. Proc. Manchester. Lit. Phil. Soc.*, 79, 13-28 (1935); *C. A.*, 30, 7981.
[14] U. S. P. 1,734,200 (1929) to A. M. Buley and H. Blumenberg, Jr.; *C. A.*, 24, 473.
[15] U. S. P. 1,354,818 (1920) to F. C. Frary; *C. A.*, 15, 152.
[16] W. Koch, *Metallwirtschaft*, 10, 69-72, 85-88 (1931); *C. A.*, 25, 2395.
[17] H. N. Warren, *Chem. News*, 66, 113-114; *J. Chem. Soc. Abs.*, 64 (II), 11 (1893). H. N. Warren, *Chem. News*, 60, 158, *J. Chem. Soc. Abs.*, 58 (I) 108 (1890).
[18] H. Gautier and G. Charpy, *Compt. rend.*, 113, 597-600 (1891); *J. Chem. Soc. Abs.*, 62 (I), 116 (1892).
[19] U. S. P. 1,423,560 (1922) to H. D. Gibbs (to du Pont); *C. A.*, 16, 3176.
[20] U. S. P. 2,125,766 (1938) to W. S. Calcott (to du Pont).

In order to reduce the high heat of reaction, Jacobson and Klipstein [21] first react bromine with scrap aluminum, and then displace the bromine with chlorine. Since bromination occurs at temperatures of 150-200°, less resistant materials of construction may be used than are necessary for chlorination of metallic aluminum. A small amount of bromine suffices to initiate the reaction, the bromine attacking the aluminum and being repeatedly replaced by the chlorine.

A similar method comprises preliminary treatment of scrap aluminum with bromoform to form a complex organic compound containing bromine and aluminum, subsequent decomposition of the complex, suitably by vacuum and heat, to yield activated aluminum, and final chlorination of the decomposed material.[22]

Aluminum chloride, to be used for refining hydrocarbon oils, may be prepared by suspending aluminum particles in the oil which is to be treated, and passing chlorine into the suspension.[23]

Reaction with Hydrogen Chloride.—The reaction of aluminum with hydrogen chloride affords a method for the preparation of aluminum chloride which, due to the low heat of reaction, does not require the special apparatus which is necessary when halogenation is effected with chlorine. The method has been much used.[24]

Gattermann [25] recommends the method for preparing aluminum chloride for use in Friedel-Crafts syntheses. The apparatus consists of a wide-mouthed bottle fitted with a two-holed cork stopper. A combustion tube is inserted in one hole, and a vent-tube from the bottle is inserted through the other hole. The other end of the combustion tube is connected by means of very short rubber tubes with two wash bottles containing concentrated sulfuric acid through which the supply of hydrogen chloride is washed. Aluminum filings are arranged in the combustion tube to a depth equal to one-third of its diameter. The end of the layer which is to be heated must not be more than 8 cm from the receiving bottle. The cork is protected from heat by means of asbestos. The tube is laid in a combustion chamber and hydrogen chloride is passed in until air is expelled. The whole length of the tube is then slowly heated. As reaction becomes established, the stream of hydrogen chloride is increased and stronger heating is used. Heating and passage of hydrogen chloride are continued until all but a small amount of the metal is volatilized. Caution should be taken to prevent choking of the apparatus by the volatilized aluminum chloride.

[21] U. S. P. 1,445,062 (1922), Brit. P. 181,285 (1922), Can. P. 237,452 (1924) all to B. H. Jacobson; *C. A.*, 18, 1037; 16, 3735; U. S. P. 1,474,479 and Brit. P. 190,668 (1923) to B. H. Jacobson (to E. C. Klipstein and Sons), *C. A.*, 17, 2039; German P. 378,372 (1923) to E. C. Klipstein and Sons. K. H. Klipstein, *Chem. Markets*, 25, 593 (1930).

[22] U. S. P. 2,023,055 (1935) to L. Valik (to Givaudan-Delawanna), *C. A.*, 30, 2714; French P. 801,532 (1936) to L. Givaudan et Cie, *C. A.*, 31, 511.

[23] British P. 22,244 (1914) to A. M. McAfee.

[24] Gore, *Phil. Mag. (4)*, 29, 541, 545 (1865); *Proc. Roy. Soc. London*, 14, 209 (1865). J. B. Cohen, *Chem. News*, 54, 305 (1886). E. Kohn-Abrest, *Bull. soc. chim. (4)*, 5, 769 (1909). L. F. Nilson and O. Petterson, *Z. phys. Chem.*, 1, 461 (1887). K. Seubert and W. Pollard, *Ber.*, 24, 2575-78 (1891). F. Stockhausen and L. Gattermann, *Ber.*, 25, 3521-3525 (1892). L. Gattermann and O. Dalert, *Monatsh.*, 40, 313 (1919). A. Schleicher, *J. prakt. Chem. (2)*, 105, 355 (1923).

[25] L. Gattermann, "Laboratory Methods of Organic Chemistry," p. 233-234, revised by H. Wieland, Macmillan, 1932.

According to Escales,[26] during the reaction of hydrogen chloride with aluminum, it is unnecessary to heat the aluminum throughout the reaction, since the action, when once started, is carried on by heat of reaction. He prepares aluminum chloride by passing a stream of dry hydrogen chloride into a tubulated ball-jar in which a large glass dish is placed, having in the center a glass tripod supporting a plate of asbestos upon which is placed about 20 g of aluminum filings. Hydrogen chloride is then passed in and the action initiated by pouring in, through the opening in the bell-jar, a small quantity of strongly heated aluminum on the asbestos plate. The action then continues until all the aluminum has been converted into chloride. It is collected from the sides of the jar and from the glass dish in about 70-75 per cent yield.

An apparatus for preparing an active grade of aluminum chloride is described by Dawson.[27] It consists of a "Pyrex" tube, bent and shaped like a funnel at one end so as to connect it lightly to a jar with an outlet for the hydrogen formed. Aluminum is placed in the tube, and the latter is surrounded by an electric furnace. After the air has been blown out of the system by a rapid stream of hydrogen, and the tube has been heated to 250°, hydrogen chloride gas is passed over the aluminum and the aluminum chloride is collected at the bottom of the jar. The reaction proceeds best in a rapid stream of hydrogen chloride at a dull red heat.

An alloy of copper and aluminum has been used to prepare aluminum chloride, hydrogen chloride extracting the aluminum without attacking the copper. Alloys containing 15 to 40 per cent of aluminum are powdered, mixed with powdered charcoal in order to prevent fusion of the remaining copper, and put into a graphite retort. When they are just below a red heat, hydrogen chloride is passed through.[28] Alloys of aluminum with tin or manganese similarly yield aluminum chloride when treated at 200-300° with hydrogen chloride.[29]

The preparation of aluminum chloride for Friedel-Crafts reactions may be effected *in situ*. Thus the reaction of aluminum with hydrogen chloride has been carried out in the presence of aluminum chloride in media capable of Friedel-Crafts synthesis.[30]

Conversion of aluminum to aluminum chloride may also be effected by suspending the finely divided metal in mineral oils which are to be refined with aluminum chloride, and then treating the suspension with hydrogen chloride.[31]

Reaction with Other Chlorides.—Aluminum chloride may be prepared by heating aluminum with chlorides of other metals. Excess of aluminum heated with lead chloride, cuprous chloride, or silver chloride readily yields aluminum chloride.[32] Mercuric chloride vapor reacts energetically

[26] R. Escales, *Ber.*, **30**, 1314-1317 (1897), *J. Chem. Soc. Abs.*, 72 (II), 407 (1897).
[27] G. A. Dawson, *J. Am. Chem. Soc.*, **50**, 133-134 (1928); *C. A.*, **22**, 1254.
[28] C. F. Mabery, *Ber.*, **22**, 2658 (1889).
[29] U. S. P. 351,194 (1886) to C. F. Mabery (to The Cowles Electric Smelting and Aluminum Co.).
[30] French P. 788,130 (1935) to Ruhrchemie A.-G., *C. A.*, **30**, 1527.
[31] British P. 22,344 (1914) to A. M. McAfee.
[32] S. D. Nicholas, *Nature*, **129**, 581 (1932); *C. A.*, **26**, 3198; *Brit. Chem. Abs.*-A, 482 (1932).

with aluminum, with separation of mercury and formation of aluminum chloride.[35]

A highly active aluminum chloride has been prepared by heating nearly to boiling 5 g of aluminum powder, 1 g of mercuric chloride, and 0.5 g of iodine in 100 cc of benzene, and passing in dry hydrogen chloride with stirring. The product is ready to use when evolution of hydrogen ceases.[34] The preparation of aluminum chloride by heating aluminum with lead or zinc chloride, or with other chlorides of a metal having less affinity for chlorine than aluminum, is covered by several patents.[35]

Weaver [36] claims the preparation of aluminum chloride by reaction of silicon chloride with aluminum. Silicon chloride is fed into and near the bottom of a bath of molten aluminum so that the chloride will rise in the aluminum. Reaction takes place with liberation of elemental silicon and formation of aluminum chloride.

The chlorine compounds of phosphorus, arsenic, antimony, and sulfur in vapor form react energetically with powdered aluminum.[37]

According to Sudborough,[38] nitrosyl chloride reacts strongly with aluminum in the cold, with evolution of nitrous gases. In the presence of an excess of nitrosyl chloride, a syrupy liquid is formed, from which aluminum chloride separates as a dark yellow precipitate.

Carbon tetrachloride may be used to chlorinate aluminum. At 180°, aluminum decomposes carbon tetrachloride, liberating carbon and forming hexachloroethane and aluminum chloride.[39]

Reaction of Chlorine with Alumina or Aluminiferous Ores

In the Absence of a Reducing Agent.—In 1811, Davy [40] reported that chlorine did not react with alumina even at red heat; according to Weber,[41] the reaction does occur at white heat, with formation of aluminum chloride in good yield. The reaction has been reported by Wasmut and Oberhoffer [42] to begin at 850°; but according to Spitzuin,[43] chlorination is observable at 800°. This investigator noted the following loss in weight of 0.73 to 0.79 g of alumina upon passing chlorine over it for one hour at a gas velocity of 10 l per hour:

temp. (°C.)	600	800	1000	1200
loss in weight (g)	0.0	0.0016	0.0083	0.0042

Kangro and Jahn,[44] however, state that the action of chlorine, sufficient to cause at least 1 per cent of alumina to react per hour, starts at

[35] A. Cossa, *N. Cim. (3)*, 3, 228 (1870).
[34] K. Bodendorf, *J. prakt. Chem.*, 129, 340 (1931), *C. A.*, 25, 2698.
[35] U. S. P. 1,541,068 (1925) to H. L. Pelser and E. C. Herthel, *C. A.*, 19, 2268; U. S. P. 1,673,495 (1928) to N. C. Christensen, *C. A.*, 22, 2815; Can. P. 256,602 (1925) to H. L. Pelser and E. C. Herthel (to Sinclair Refining Co.).
[36] U. S. P. 1,241,788 (1917) to V. M. Weaver, *C. A.*, 12, 206.
[37] C. Matignon, *Compt. rend.*, 130, 1293 (1900).
[38] J. J. Sudborough, *J. Chem. Soc.*, 99, 655-664 (1911).
[39] E. V. Zappi, *An. Soc. Quim. Argentina*, 2, 217-228 (1914); *J. Chem. Soc. Abs.*, 108 (1) 114 (1915).
[40] H. Davy, *Ann. Chim. Phys.*, 79, 9 (1811).
[41] R. Weber, *Pogg. Ann.*, 112, 621 (1861).
[42] R. Wasmut and P. Oberhoffer, *Arch. Eisenhüttenwesen*, 2, 833 (1929).
[43] V. Spitsuin, *Z. anorg. allgem. Chem.*, 189, 337-56 (1930); *C. A.*, 24, 5249.
[44] W. Kangro and R. Jahn, *Z. anorg. allgem. Chem.*, 210, 325-336 (1933); *C. A.*, 27, 1693.

1200°. These investigators are of the opinion that the small loss by weight which occurs at 800° does not indicate conversion to aluminum chloride. According to Fischer and Gewehr,[45] aluminum oxychloride is also formed during the reaction.

In the Presence of a Reducing Agent.—When chlorine is passed over a heated mixture of alumina and carbon, the alumina is reduced to aluminum by the carbon present and reaction occurs readily. According to Spitzuin,[46] reaction in the presence of an excess of carbon proceeds according to the equation:

$$2Al_2O_3 + 6C + 6Cl_2 \qquad 4AlCl_3 + 6CO + Q_1$$

with Q_1 equal to -47 kcal. Fischer and Gewehr [45] give the value of Q_1 as -47 kcal, and report that in the presence of less carbon the reaction is

$$2Al_2O_3 + 3C + 6Cl_2 = 4AlCl_3 + 3CO_2 + Q_2$$

with Q_2 equal to $+77$ kcal. Wurster [46] has pointed out that since, after its initiation, the reaction may be effected commercially without external heating, the second equation is the more probable.[47] It has been pointed out by McAfee,[48] however, that carbon monoxide is one of the reaction products of the chlorination of briquets containing approximately 82 per cent bauxite and 18 per cent carbon.

Alumina in the presence of carbon begins to react with chlorine at about 700°.[49] The action of chlorine on a mixture consisting of two parts of alumina and one part of coal at a gas velocity of 10 l per hour has been reported to give the following results.[50]

temp. (°C.)	600	700	800	1000
% reacted oxide per hour	0.00	0.04	2.08	86.15

Improved conversion is secured by powdering the mixture of alumina and carbon. Briquetting aluminiferous material with carbon increases the rate of chlorination,[51] the porosity of the briquettes facilitating the attack of the chlorine.

The production of aluminum chloride by reaction of chlorine with alumina was first described by Oersted [52] and was frequently reported by other early investigators.[53]

The use of bauxite as the aluminiferous material has been developed principally by the Gulf Refining Company who first attempted the commercial production of aluminum chloride in 1915. In 1929, McAfee [54]

(*Text cont'd. on p. 853*)

[45] W. Fischer and R. Gewehr, *Z. anorg. allgem. Chem.*, 209, 17-32 (1932).
[46] C. Wurster, *Z. angew. Chem.*, 43, 877-880 (1930).
[47] German P. 551,400 (1926) to I. G.; *C. A.*, 25, 5521.
[48] A. M. McAfee, *Ind. Eng. Chem.*, 21, 670-673 (1929).
[49] R. Wasmut and P. Oberhoffer, *Arch. Eisenhuttenwesen*, 2, 833 (1929).
[50] V. Spitsuin, *Z. anorg. allgem. Chem.*, 189, 337-66 (1930); *C. A.*, 24, 5249.
[51] V. I. Spitsuin and O. M. Gvosdeva, *Z. anorg. allgem. Chem.*, 196, 289-311 (1931); *C. A.*, 25, 2381.
[52] H. C. Oersted, *Overs. Danske Selsk. Fork.*, 1824/1825, 15; *Pogg. Ann.*, 5, 132 (1825).
[53] J. Liebig, *Ann.*, 17, 43 (1836). F. Wohler, *Pogg. Ann.*, 11, 148 (1827); *Ann.*, 53, 422 (1845). R. Bunsen, *Pogg. Ann.*, 92, 648 (1854).
[54] A. M. McAfee, *Ind. Eng. Chem.*, 21, 670-673 (1929); *Chem. Met. Eng.*, 36, 422-424 (1929); *Refiner*, 8, (8) 87 (1929); *J. Chem. Education*, 7, 2376-2382 (1930); *cf.* L. M. Aycock, *Ind. Eng. Chem.*, 22, 430 (1930); M. Naphthali, *Petroleum Z.*, 26, 55-56 (1930); I. N. Strukov, *Neftyanoe i slanczevoe Chozjajstva*, 5, 246-250 (1929), *C. Z.*, 1924 I, 2623.

Table 42. Treatment of Alumina or Aluminous Ore or Clay with Carbonaceous Material and Chlorine

Reaction	Reference
Bauxite + molasses, asphalt, or petroleum residue, chlorinated at 870-980°.	U. S. P. 1,217,471 (1917) to A. M. McAfee, *C. A.*, 11, 1128.
Alumina coked with molasses in revolving chamber heated to 700-800°, treated with preheated chlorine.	U. S. P. 1,699,239 (1929) to W. F. Downs, *B.C.A.*-B, 433 (1929).
Dehydrated bauxite heated with carbon in an electric furnace to yield aluminum carbide; then chlorination.	U. S. P. 1,270,236 (1918) to D. F. Smith and H. Essex, *C. A.*, 12, 1880.
Bauxite + coal, coke, or asphalt, heated to coking temperature on a conveyer, removed from conveyer; then chlorinated.	U. S. P. 1,508,451 (1924) to G. W. Gray and F. W. Hall, *C. A.*, 18, 3687.
Bauxite + carbonaceous material; simultaneous coking and purifying by heating and chlorinating at a relatively low temperature; subsequent chlorination at higher temperature.	U. S. P. 1,600,316 (1926) to R. J. Dearborn (*C. A.*, 20, 3542; U. S. P. 1,605,098 (1926) to R. J. Dearborn, *C. A.*, 21, 160; Can P 257,752 (1926) to R. H. McKee, *C. A.*, 20, 2294
Bauxite + C is placed in reaction chamber so that mixture is denser at the walls of chamber than at other points; halogenation with mixture of chlorine and air at 600-700°.	U. S. P. 1,690,990 (1928) to A. M. McAfee and G. I. Roberts (to Gulf Refining Co.), *C. A.*, 23, 487.
Fine-grained mixture of bauxite and carbon projected by a jet of Cl containing some O and N.	U. S. P. 1,867,672 (1932) to A. M. McAfee (to Gulf Refining Co.), *C. A.*, 26, 5181.
Alumina, bauxite, or clay + coal; preliminary chlorination at below 350°; then at about 900°.	Japanese P. 109,733 (1935) to Mitsui Kozan K. K., *C. A.*, 29, 4910
Bauxite or clay + C; preliminary chlorination at 300-450°; then at 900°.	U. S. P. 1,147,832 (1915) to F. von Kugelgen and G. O. Seward, *C. A.*, 9, 2572.
Chlorination of a mixture of alumina + carbon in suspension.	Can. P 222,315 (1922) to G. H. King and G. I. Roberts, *C. A.*, 16, 4022.
Alumina + carbon; chlorine preheated by passing over ignited C.	Can. 222,317 (1922) to L. S. Abbott, *C. A.*, 16, 4022; U. S. P. 1,308,885 (1919) to L. S. Abbott, *C. A.*, 13, 2262.
Alumina + excess of C is passed through a retort and contacted with Cl; hot gases resulting from excess of C used to heat retort.	U. S. P. 1,619,022 (1927) to F. W. Hall, *C. A.*, 21, 1336; Can. P. 259,218 (1926) to G. W. Gray, *C. A.*, 20, 3542; Can P 259,219 (1926) to G. W. Gray and F. W. Hall, *C. A.*, 20, 3542.
Bauxite or clay with C and Cl are heated in an electric furnace having a locally heated zone.	U. S. P. 1,752,936 (1930) to W. R. Austin and J. N. Smith (to Farley G. Clark), *C. A.*, 24, 2554.
Feeding a preheated mixture of finely powdered alumina and C together with preheated chlorine through a heated reaction chamber.	U. S. P. 1,268,015 (1918) to G. H. King and G. I. Roberts, *C. A.*, 12, 1917.
Bauxite with coke chlorinated in counter-current.	U. S. P. 1,568,181 (1926) to G. L. Pruhud and H. Henderson, *C. A.*, 20, 849.
Finely divided mixture of coke and bauxite passed downwardly against an ascending current of Cl, O, and N.	U. S. P. 1,823,450 (1931) to A. M. McAfee (to Gulf Refining Co.), *C. A.*, 26, 1072.
Mixture of oxides of Al, Fe, and Mg coked with calcined carbon black, chlorinated at 700-900°.	K. Yamamoto, H. Ishikawa, and K. Machida, *J. Soc. Chem. Ind. Japan*, 39, Suppl. binding 312-314 (1936), *C. A.*, 31, 527.
Alumina + tar is heated to form briquettes which are then chlorinated.	N. N. Voronin and I. S. Galinker, *J. Chem Ind. (Moscow)*, 7, 142-149 (1930); *C. Z.*, 1930 II, 783, *C. A.*, 25, 4065.
Chlorine passed through alumina mixed with peat or sawdust.	French P. 636,339 (1927) to I. G., *C. A.*, 23, 244.
Alumina + sawdust, peat, or coke, coked to form briquettes; chlorination temperature maintained by heat of reaction.	German P. 531,400 (1926) to I. G., *C. A.*, 25, 5521.
Chlorination of bauxite in presence of activated C.	U. S. P. 1,509,605 (1924) to R. H. McKee *C. A.*, 18, 3687; U. S. P. 1,544,328 (1925) to A. M. McAfee, *C. A.*, 19, 2780; Can. P 257,752 (1926) to R. H. McKee, *C. A.*, 20, 2294.
Finely divided bauxite is coked with coal and chlorinated.	Can. P. 222,309 (1922) to A. M. McAfee, *C. A.*, 16, 4021.

Table 42.—*(Continued)*

Reaction	Reference
Bauxite + C is treated with a mixture of Cl and returned gases from $AlCl_3$ condensers or other gases containing an oxide of C, and then treated with Cl.	U. S. P. 1,578,052 (1926) to A. M. McAfee, *C. A.*, 20, 1695.
Alumina ash is contacted with water; liquid is removed; and the aluminous material coked with an asphaltic substance; subsequent treatment with chlorine.	U. S. P. 1,865,008 (1932) to M. M. Holm (to Standard Oil Co. of Cal.), *C. A.*, 26, 4422.
Powdered aluminum ore is coked with acid sludge from oil refining and then chlorinated.	Can. P. 270,384 (1927) to F. W. Hall, *C. A.*, 21, 3428; U. S. P. 1,540,766 (1925) to F. W. Hall, *C. A.*, 19, 3587; *cf.* Russian P. 31,424 (1933) to M. E. Mandenov and A. M. Monoszon, *C. A.*, 28, 2856.
Chlorination of bauxite mixed with soft coal, pitch, or acid sludge.	U. S. P. 1,503,648 (1924) to F. W. Hall, *C. A.*, 18, 2948.
Pulverized alumina and finely divided C and Cl injected into a combustion and reaction chamber.	U. S. P. 1,366,826 (1921) to C. M. Alexander, *C. A.*, 15, 1059.
Alumina, C, and Cl, fed into revolving, externally heated, fused silica reaction chamber.	U. S. P. 1,862,298 (1932) to B. E. Carl, *C. A.*, 26, 4139.
Use of vertical shaft furnace on counter-current principle for production of $AlCl_3$ from alumina C, and Cl.	German P. 525,186 (1927) to J. Brode and C. Wurster (to I. G.), *C. A.*, 25, 4365.
Interaction of alumina, C, and Cl in a reaction zone of special apparatus; condensation of formed $AlCl_3$ in a condensing zone, zones maintained under such pressure that $AlCl_3$ is obtained as liquid in the condensing zone.	U. S. P. 2,048,987 (1936) to Gulf Oil Corp., *C. A.*, 30, 6517.
Cl and O diluted with air is passed through a pervious charge of aluminous material and carbon at a temperature sufficient to form vapors of $AlCl_3$.	U. S. P. 2,084,290 (1937) to A. M. McAfee (to Gulf Oil Corp.).
Chlorine and oxygen is passed through pervious charge of alumina and carbon at a temperature sufficient to form vapors of $AlCl_3$.	U. S. P. 2,084,289 (1937) to A. M. McAfee and J. A. Tryon (to Gulf Oil Corp.).
Alumina, C, and Al treated at 50° with Cl, heat generated by reaction of Al with Cl effects reduction of alumina with C.	Brit. P. 163,975 (1920) to Aluminum Co., *C. A.*, 16, 144; Can. P. 216,244 (1922) to F. C. Frary, *C. A.*, 16, 1491; U. S. P. 1,354,818 and French P. 534,839 to Aluminum Co.
Alumina + carbonaceous material + small amount molten Al; the $AlCl_3$ vapors formed from Cl and Al supply heat for further reactions.	British P. 343,785 (1930) to Imperial Chemical Industries, Ltd., and J. W. Pritchard, *C. A.*, 25, 4668.
Coke containing Al_2O_3 is treated in a vertical retort with upflowing Cl_2 and O in amount sufficient to maintain the reaction temperature.	U. S. P. 1,887,566 (1932) to W. H. Shiffler and W. P. Anderson (to Standard Oil Co. of California.); *B.C.A.*-B, 828 (1933).
Al ore and highly porous coking material are treated with diluted chlorinating agent to remove S of the ore.	Austrian P. 114,181 (1929) to I. G.; *C. Z.*, 1930 *I*, 1517.
Alumina and carbon heated in a stream of Cl or in a static atmosphere of Cl yields $AlCl_3$, O, and CO_2; temperature at which reaction started decreased with increased proportion of C.	N. M. Stover and C. Constnatinescu, *Can. J. Research*, 14B, 328-335 (1936); *C. A.*, 31, 60.
Heat of reaction calculated for formation of $AlCl_3$ from amorphous carbon and chlorine at 600°; the reaction producing CO was considered to be principal reaction.	W. D. Treadwell and L. Terebrat, *Helv. Chim. Acta*, 15, 1053-1066 (1932), *C. A.*, 27, 657.
Vapors of petroleum + chlorine are distilled into retort containing alumina heated to redness.	H. N. Warren, *Chem. News*, 55, 192 (1887).
Hot alumina treated in retort with hydrocarbon vapors; material then treated with Cl.	U. S. P. 1,713,968 (1932) to H. I. Lee and C. W. Humphrey, *C. A.*, 23, 3546.
Hydrogen and large excess of chlorine passed over hot mixture of alumina and carbon; heat of reaction between H and Cl effects sublimation of the metal chlorides.	German P. 455,266 (1924) to Ver. f. Chem. Mettalurg. Production, *B.C.A.*-B, 283 (192

Table 42.—*(Continued)*

Reaction	Reference
Alumina (heated at 1600-2000° to render it anhydrous), mixed with C and then treated with Cl; CO is formed by exothermic reaction of C with the Al_2O_3.	U. S. P. 1,375,116 (1921) to M. Shoeld, *C. A.*, 15, 2700.
Producer furnace for heating $AlCl_3$ stills.	U. S. P. 1,440,857 (1923) to G. D. White, *C. A.*, 17, 1182.
Apparatus for manufacture of $AlCl_3$ from alumina, C, and Cl comprises a retort connected to Cl producer, and a furnace for heating the retort.	U. S. P. 1,512,419 (1924) to G. W. Gray, *C. A.*, 19, 155.
Apparatus for manufacture of $AlCl_3$ from alumina, coke, and Cl comprises a retort having an outlet for spent material which is sealed with ash.	U. S. P. 1,468,682 (1923) to F. W. Hall, *C. A.*, 17, 3008; U. S. P. 1,530,493 (1925) to F. W. Hall, *C. A.*, 19, 1018.
Retort for manufacture of $AlCl_3$ is lined with a mixture of clay and alkali-metal silicate.	U. S. P. 1,617,606 (1927) to E. R. Wolcott, *C. A.*, 21, 1169; Can. P. 270,381 (1927) to E. R. Wolcott, *C. A.*, 21, 3428.
Natural double silicates containing alumina are admixed with reducing agents at elevated temperature in an atmosphere of Cl.	German P. 267,876 (1913) to R. van der Leeden, *C. A.*, 8, 1491.
Clay and reducing agent + Cl yields $AlCl_3$ and $SiCl_4$.	German P. 399,454 (1924) to Weaver Co., *C. Z.*, 1924 II, 1732.
Al silicate material + oil-shale or low grade coal first heated to distil hydrocarbons and residue is heated with Cl.	Can. P. 217,051 (1922) to E. R. Wolcott, *C. A.*, 16, 1839.
Al ore containing Si compound are chlorinated to yield vapors of Al_2Cl_6 and $SiCl_4$; Al_2Cl_6 vapors are condensed first.	Can. P. 270,382 (1927) to E. R. Wolcott, *C. A.*, 21, 3428; U. S. P. 1,633,835 (1927) to E. R. Wolcott, C. A., 21, 2763.
Clay + coal is chlorinated and vapors led into a fused $AlCl_3$-NaCl mass which abstracts $AlCl_3$ and iron chloride.	German P. 628,953 (1936) to Consolidirte Alkali-werke, *C. A.*, 30, 6144.
Kaolin + coal chlorinated in a kiln subdivided by baffles; downward movement of the mass; upper section mixture is heated to about 850°; chlorination in lower section.	Russian P. 31,426 (1933) to A. P. Khozin, *C. A.*, 28, 2856.
Al silicates are treated with a gaseous chlorinating agent containing H.	French P. 688,563 (1930) to O. M. Henriques and T. A. Thomsen, *C. A.*, 25, 676.
Hot calcined clay is introduced into chlorinating furnace; heated in a stream of air for 15 minutes to burn the C to CO, and then chlorinated for 8-10 hours.	I. E. Adadurov, *J. Chem. Ind. (Moscow)*, 6, 1527-1530 (1929); *C. A.*, 24, 5941.
Kaolin is pretreated with warm HCl or HNO_3 previous to chlorination.	P. P. Fedoteev and A. A. Tschishik, *Trans. State Inst. Appl. Chem., U.S.S.R.*, No. 20, 59-68 (1934), *B.C.A.*-B, 848 (1935).
Briquettes of clay, coke, and tar are heated at 400° to remove volatile material and then treated with 4:1 Cl_2-air at 900°; Fe content of clay may be eliminated by treating in a stream of HCl at 900°.	A. Kucsorowski, *Przemysl Chem.*, 20, 221-228 (1936), *B.C.A.*-B, 541 (1937).
Kaolin + 2% of NaCl or $Na_2B_4O_7$ chlorinated at 650°.	Ya. E. Seferovich, *J. Chem. Ind. (Moscow)*, No. 10, 62-64 (1934); *C. A.*, 29, 1213.
Clay + tar briquettes are chlorinated at 600°; only 45% of Cl is used to chlorinate Al_2O_3; addition of alkali chlorides does not improve yields; chlorination products of Si, Fe, and Ti also formed.	N. N. Voronin and I. S. Galinker, *J. Chem. Ind. (Moscow)*, 7, 143-149 (1930); *C. Z.*, 1930 II, 783; *C. A.*, 25, 4665.
Reduction of clay in presence of chlorine and reducing agent.	German P. 397,073 (1924) to Gulf Refining Co., *C. Z.*, 1924 II, 1389.
Clay first freed from Fe by heating in current of HCl gas at 400-900°; chlorination of alumina with Cl begins at 600°; addition of $SiCl_4$ to Cl suppressed chlorination of SiO_2.	V. I. Spitsyn and O. M. Gvosdeva, *Z. anorg. allgem. Chem.*, 196, 289-311 (1931); *C. A.*, 25, 2381.
Raw materials containing alumina and silicic acid mixed with brown coal, briquetted, heated to 700-800° and reacted with Cl and $SiCl_4$.	U. S. P. 1,866,731 (1932) to K. Staib (to I. G.), *C. A.*, 26, 4697; Brit. P. 305,578 (1928) to I. G., *C. A.*, 23, 4782; German P. 502,322 (1928) to I. G., *C. A.*, 24, 4904.
Coal ash containing clay is chlorinated to yield $AlCl_3$, $FeCl_3$, and $SiCl_4$.	P. P. Budnikov and M. I. Nekrich, *Chem. Ztg.*, 56, 681-683 (1932); *C. A.*, 26, 6073.

Table 42—*(Concluded)*

Reaction	Reference
Chlorine is passed into a mixture of crushed rocks or clay and carbon; chlorides of Al, Si, and Fe are obtained.	Japanese P. 101,515 (1933) to K. Kitaoka, *C. A.*, **28**, 5186.
Potassium aluminum silicate + only enough C and Cl to convert the K and the Al of the double silicate to chlorides. The SiO_2 remains practically undecomposed.	German P 289,909 (1914) to Siemens and Halske, Akt.-Ges.; *C. A.*, **10**, 2622.
Minerals rich in plagioclases of the labradorite-anorthosite series are heated to 600-1000° with a small amount of C and at the same time supplied with Cl or HCl gas	U. S. P 1,302,852 (1919) to O Reyner and V. M Goldschmidt, *C. A.*, **13**, 1907.
Carbonaceous shale is heated sufficiently to effect destructive distillation and residue is treated with Cl.	U S P. 1,506,104 (1924) to E R. Wolcott, *C A*, **18**, 3257.

described the process which has been developed. A survey of the developments in the commercial preparation of aluminum chloride from bauxite, clay and other aluminiferous ores, admixed with various carbonaceous materials is given in the subsequent pages.

Reaction of Alumina or Aluminiferous Ores with Hydrogen Chloride

Although chlorination of alumina may be effected by treatment with hydrogen chloride, the reaction requires much higher temperatures than does halogenation with chlorine. At 1200°, for one hour with a hydrogen chloride gas velocity of 11.5 liters per hour the loss by weight of 0.8-1.0 g of alumina is only 0.054 g. The sublimed product, due to hydrolysis, is a mixture of alumina and aluminum chloride. Reaction is incomplete, since an equilibrium between water vapor, anhydrous chloride, oxide, and hydrogen chloride is set up or approached.[55] The action of hydrogen chloride on alumina was studied by variation of the vapor pressure of the gases at over 1000°, and the reaction was found to proceed according to the equation [56]:

$$Al_2O_3 + 6HCl \rightleftharpoons 2AlCl_3 + 3H_2O - 68 \text{ cal.}$$

The reaction in the presence of carbon was noted in 1855 by Deville,[57] who noted that although hydrogen chloride may be used to chlorinate a mixture of alumina and carbon, very high temperatures are necessary. According to Spitzuin,[55] carbon has no effect on the temperature at which reaction sets in; but it does accelerate the reaction in that it unites with the oxygen or water produced by the main reaction, and thus prevents equilibrium from being set up. At 800° for one hour at a hydrogen chloride velocity of 11.5 liters per hour, 2.06 per cent of the alumina is affected; at 1000°, the conversion is 35 per cent. In treatment of kaolin earth or argillaceous earth coal mixtures, the raw material must first be freed of iron by heating in a current of hydrogen chloride at 400-900°;

[55] V. Spitsuin, *Z. anorg. allgem. Chem.*, **189**, 337-366 (1930); *C. A.*, **24**, 5249.
[56] W. Fischer and R. Gewehr, *Z. anorg. allgem Chem.*, **209**, 17-32 (1932), *C. A.*, **27**, 457.
[57] H. Sainte-Claire Deville, *Ann. chim. phys. (3)*, **43**, 23 (1855).

for the chlorination of the alumina in the ore with hydrogen chloride, briquetting and an excess of carbon are advantageous.[58]

The following references cite the use of hydrogen chloride for chlorination of alumina or aluminiferous ores:

Clay is heated with strong hydrochloric acid to produce an aqueous solution of aluminum chloride containing chlorides of other metals Evaporation yields hydrated aluminum chloride crystals and aluminum oxide.	Brit P 130 164 (1918) to R Welford, *C A*, 14, 211
The mother liquor from a similar process is used for washing the crystalline precipitate and to absorb hydrogen chloride gas from the calcination of the hydrated aluminum chloride produced	Brit P 205,563 (1922) to Chemische Fabrik Griesheim-Elektron, *C A*, 18, 1037
A container for the treatment of clay with hydrochloric acid is described together with the procedure used to produce in a single pass, a clear finished liquor of aluminum chloride corresponding to 120-130 g aluminum oxide per liter	Can P 284 708 (1928) to O Jonas, K Weger and G Trebitsch (to I G) *C A*, 23, 038
Finely ground residues from coal mining, schists slags kaolins and siliceous bauxites are treated with hydrogen chloride gas under pressure to produce aluminum chloride	French P 782 369 (1935) to L Freling and J Dorren, *C A*, 29, 7026
The production of hydrated aluminum chloride as an intermediate in the preparation of alumina is attained by treating clay, argillaceous slate, or bauxite with hydrogen chloride The chlorides are precipitated from solution by adding the hydrogen chloride gases produced from the subsequent calcination process	Brit P 217,568 (1923) to Hoganas - Billesholms Aktiebolag, *C A*, 19, 383
Aluminum oxide is heated to redness in a tubular earthenware retort Petroleum vapor saturated with hydrogen chloride gas is led through the retort to produce anhydrous aluminum chloride which is condensed from the exit gases	H N Warren *Chem News* 55, 192 *J Chem Soc Abs*, 52, 702 (1887)
Hot bauxite is treated with a mixture of hydrogen chloride and naphthalene gases to evolve anhydrous aluminum chloride	A Faure *Compt rend* 107, 339-340 (1888) *J Chem Soc Abs* 54, 1250 (1888)
Bauxite or alunite residue is treated with hydrogen chloride gas in the presence of carbon at a temperature above 1500° to yield anhydrous aluminum chloride	U S P 1,698 238 (1929) to C G Miner *C A*, 23, 1223
A two-step process consists in the preliminary reduction of the ore with carbon in an electric furnace The reduced material is then contacted with dry hydrogen chloride at a low red heat to produce anhydrous aluminum chloride	L Burgess, *Trans Am Electrochem Soc* 47, (preprint) (1925) *C A* 19, 1840
Another two-step process involves the heating of clay, bauxite shale, or other aluminum silicates with coal or sawdust, the reduced residue being subsequently treated with a mixture of dry hydrogen chloride and chlorine to yield anhydrous aluminum chloride	U S P 1 528 039 (1925) to E R Wolcott, *C A* 19, 1476
The production of chlorine for a process of preparing aluminum chloride similar to the above described method can be accomplished by first treating heated magnesium oxide with hydrogen chloride gas Air is then contacted with the magnesium chloride resulting to produce free chlorine and regenerate the oxide	U S P 1 612,686 (1926) to E R Wolcott *C A* 21, 630
Aluminum oxide, coke, nitrogen, and hydrogen chloride react at 1400-2000° to produce anhydrous aluminum chloride The ratio of hydrogen chloride to nitrogen should be six to one	U S P 1,875,348 (1932) to C G Miner, *Brit Chem Abs*-B, 625 (1933)

Alumina or Aluminiferous Ores and Metallic Chlorides

Instead of chlorine, certain anhydrous metallic chlorides may be heated with alumina, bauxite, or other aluminous ores to yield aluminum chloride. Chlorides of metals which have a lesser affinity for chlorine than does aluminum may be used. Although sodium chloride is the cheapest source of chlorine, its volatility detracts from its usefulness for this purpose. Only a few instances of its application have been noted. In one process, a mixture of coke, sodium chloride, alumina, bauxite, clay or slag makes up a blast furnace charge for the manufacture of aluminum

[58] V. Spitsuin and O M. Gvosdeva, *Z. anorg allgem. Chem.*, 196, 289-311 (1931), *C A.*, 25, 2381

chloride. During the reaction, carbonyl chloride is formed, and this reacts with the aluminum to yield aluminum chloride.[59] A modification of this method involves calcining clay or aluminum silicate with sodium chloride at 1200° to produce aluminum chloride and sodium silicate, and the use of free nitrogen to sweep out the volatile aluminum chloride.[60] This process was later investigated by Hackspill and Salomon,[61] who were unable to obtain the results which had been claimed. A somewhat more complicated process specifies heating a mixture of calcined clay and sodium chloride or potassium chloride in a rotary furnace to bright redness and passage of arsenous oxide over the mass to form sodium or potassium aluminate, silica, and arsenic trichloride. The aluminate is dissolved out with water, and the solution is treated with carbon dioxide to precipitate aluminum hydroxide. This is then mixed with coke and, if desired, sodium chloride and formed in briquets which are heated and treated with gases containing chlorine, obtained from the arsenic trichloride. Aluminum chloride, or the double salt sodium aluminum chloride, is formed and distilled.[62] The production of sodium aluminum chloride by heating briquets consisting of alumina, sodium chloride, and carbon in a stream of chlorine had been previously described.[63]

The use of calcium chloride as the halogenating component is claimed in several patents issued to Booth and Marshall.[64] Aluminiferous material such as clay, bauxite, or feldspar is mixed with calcium chloride and carbon, and the mixture (containing silica) is heated to 1200° or above in an electric furnace to form aluminum chloride and calcium silicate. Ralston [65] has calculated that for practical operation this process requires 2.30 kwh of electrical energy to produce 1 pound of aluminum chloride, and has indicated that the method merits further investigation. A few years later, Mardick [66] claimed that when bauxite is used as the aluminous material, the method affords a means of obtaining not only aluminum chloride, but also calcium carbide. A further modification of this process involves the use of carbon dioxide as the carbonaceous material.[67] Aluminum-containing materials are first treated with aluminum chloride or hydrogen chloride in an amount insufficient for the formation of aluminum chloride. The product is then heated in an autoclave under pressure together with calcium chloride or another alkaline-earth metal chloride in the presence of carbon dioxide. The products are aluminum chloride and alkaline-earth carbonate.

In 1889 Faure [68] claimed that the action of ferric chloride on a heated mixture of alumina and carbon resulted in volatilization of aluminum

[59] U. S. P. 1,525,041 (1925) to C. E. Parsons and S. Peacock, *C. A.*, **19**, 1035.
[60] U. S. P. 1,507,700 (1924) to S. Peacock, *C. A.*, **18**, 3457.
[61] L. Hackspill and J. Salomon, *Chim. et Ind. Special Number*, 415C (1928).
[62] British P. 123,243 (1918) to E. E. and P. C. Dutt; *C. A.*, **13**, 1520.
[63] British P. 10,011 (1856) to Graf R. de Monteglas; *C. Z.*, 1857, 424.
[64] U. S. P. 1,392,043-5 (1921), *C. A.*, **16**, 318, and Can. P. 231,954-5 (1922), to H. S. Booth and G. G. Marshall.
[65] O. C. Ralston, "Anhydrous Aluminum Chloride," Bureau of Mines Tech. Paper 321 (1923).
[66] U. S. P. 1,600,899 (1926) to J. R. Mardick (to Union & Carbon Research Laboratories), *C. A.*, **20**, 3542; *cf.* U. S. P. 1,528,039 (1920) to E. R. Wolcott (to The Texas Co.).
[67] Russian P. 23,387 (1931) to A. A. Khakin and V. L. Lukashev, *C. A.*, **26**, 2286.
[68] German P. 55,096 (1889) to C. A. Faure.

chloride admixed with ferrous chloride; the chlorides of copper, nickel, cobalt, antimony, or bismuth were also claimed to be suitable for the reaction. More recently, Miner and Baird [69] described the production of aluminum chloride and the free metal corresponding to the halogenating component by heating to over 1000° a mixture of alumina, carbon, and a chloride of lead, carbon, iron, or zinc. The formed aluminum chloride sublimes and the added chloride is reduced to metal. If clay is used instead of alumina, a silicide is formed instead of the metal.

Aluminum chloride may be produced by electrolyzing zinc chloride or another metal chloride in contact with carbon and alumina, the nascent chlorine acting upon the alumina to yield aluminum chloride, containing possibly a small amount of zinc chloride. This impurity is separated by resubliming.[70]

Reaction of Alumina or Aluminiferous Ores with Sulfur Chlorides or a Mixture of Sulfur and Chlorine

Alumina is readily converted into aluminum chloride when heated with sulfur monochloride.[71] More effective is a mixture of chlorine with sulfur monochloride, in that the mixture possesses both chlorinating and reducing properties and reaction is effected at comparatively low temperature.[72] In one method [73] clay is first heated to about 900° to drive off water, and sulfur chlorides and chlorine are passed over the material at a temperature of 400-450° until substantially all the iron and titanium contained is chlorinated and volatilized. The temperature is then raised to 700° to effect chlorination of the alumina, and to 750-850° to halogenate the aluminum silicate. Another process [74] involves passage of chlorine containing sulfur monochloride over a heated mixture of alumina or clay with carbon. The first product is a sublimate containing an addition product of sulfur monochloride with aluminum chloride; the two chlorides are separated by distillation, preferably under reduced pressure.

Sulfur, instead of carbon, may be used as the reducing material in the preparation of aluminum chloride from alumina or aluminum-containing ores. Hall [75] treats powdered alumina with heated sulfur and chlorine and obtains aluminum chloride and sulfur dioxide as products. It is claimed that the reaction is highly exothermic and that it takes place at lower temperatures than carbon reduction. Since sulfur chloride and aluminum chloride in the presence of chlorine form a double compound, $AlCl_3.SCl_4$, a substance which is mushy and difficult to handle, particular care must be paid to avoid formation of this compound by

[69] U. S. P. 1,997,629 (1935) to C. G. Miner (to D. Baird), *Brit. Chem. Abs.*-B, 416 (1936), *C.* 1 29, 1563; Brit. P. 451,969 (1935) to C. G. Miner and D. Baird, *Brit. Chem. Abs.*-B, 1206 (1936) French P. 784,178 (1935) to C. G. Miner and D. Baird, *C. A.*, 30, 259

[70] U. S. P. 1,343,682 (1920) to P. Danckwardt, *C. A.*, 14, 2299; British P. 168,643 (1920) to P. Danckwardt, *C. A.*, 16, 387.

[71] R. D. Hall, *J. Am Chem. Soc.*, 26, 1235-1250 (1904), *J. Chem. Soc. Abs.*, 86 (II), 824 (1904) U. S. P. 1,480,021 (1924) to J. G. Stafford, R. H. Gardner, and E. B. Phillips, *C. A.*, 18, 2060

[72] C. Matignon and F. Bourion, *Compt. rend.*, 138, 631-633 (1904), *J. Chem. Soc. Abs.*, 86 (II) 840 (1904).

[73] U. S. P. 1,858,272 (1932) to L. G. Jenness (to Intermetal Corp.), *C. A.*, 26, 3882.

[74] British P. 176,511 (1922) to Consortium f. Elektrochemische Industrie-Ges., *C. A.*, 17, 857.

[75] U. S. P. 1,422,868 (1923), *C. A.*, 16, 3176; U. S. P. 1,405,115 (1922); *C. A.*, 16, 1135—both to F. W. Hall.

causing every bit of sulfur chloride formed to react in passing through the chlorinator.[76] Haglund[77] first treats alumina with such amounts of a material containing sulfur that an aluminum sulfide melt is formed. This is then chlorinated with chlorine, hydrogen chloride, or chlorides of sulfur or phosphorus. The sulfur-containing materials may be sulfides of iron, copper, or zinc, or ores containing metal sulfides.[78]

Sulfur or sulfur compounds may be used in connection with carbonaceous material as added reducing agent. Clark[79] claims reaction between an alumina-bearing material, a sulfurous material such as sulfur dioxide, or carbon disulfide, an excess of carbonaceous material, and hydrogen chloride under the influence of heat.

Mardick[80] reacts chlorine and carbon disulfide with alumina or bauxite mixed with lime at a temperature of about 750-1200°. It is claimed that the lime combines with the sulfur dioxide produced by the action of carbon disulfide on the alumina.

Reaction of Aluminous Ores or Clay with Carbon Monoxide and Chlorine or with Phosgene

The use of carbon monoxide as the reducing agent in the production of aluminum chloride from aluminum ores has been the subject of a number of investigations. Wurster[81] describes a process involving the use of a shaft furnace on the counter-current principle. Carbon monoxide and chlorine are fed into the bottom, anhydrous clay or bauxite is fed continuously at the top, and a residue high in silica is removed continuously from the bottom. Aluminum chloride and carbon dioxide leave the top, passing to cooled cylinders having discharge devices. No external heating of the furnace is necessary. At first the contents are heated to about 500° by producer gas, then cold carbon monoxide and chlorine are blown in. The heat of chlorination is sufficient to maintain the internal temperature of the furnace at about 900°. When material low in aluminum is present in the reaction chamber, the temperature drops. To avoid this, chlorine must first be converted to phosgene, and then fed into the bottom of the furnace at 500°. The furnace itself is so built that it resists corrosion and dissipation of heat, having tight outside jackets of iron and a lining of ceramic material stable to chlorine and aluminum chloride at high temperatures and insulation of kieselguhr. The process, as covered by patents to Brode and Wurster, is applicable to the production of aluminum chloride from alumina, aluminum silicate, kaolin, or bauxite.[82] Producer gas, or a gas mixture containing carbon monoxide, hydrogen,

[76] O. C. Ralston, "Anhydrous Aluminum Chloride," Bureau of Mines Technical Paper 321, Washington, 1923.

[77] German P. 521,339 (1925) to T. R. Haglund, *C. A.*, 25, 2819; Swiss P. 120,514 (1925) to T. R. Haglund, *Brit. Chem. Abs.*-B, 815 (1928).

[78] Swedish P. 60,424 (1926) to T. R. Haglund, *C. A.*, 20, 2231.

[79] U. S. P. 1,851,272 (1932), to C. B. Clark (to General Chemical Co.), *C. A.*, 26, 3078.

[80] U. S. P. 1,325,203 (1919) to J. R. Mardick, *C. A.*, 14, 454.

[81] C. Wurster, *Z. angew. Chem.*, 43, 877 (1930); *Chem. Ztg.*, 55, 917 (1931).

[82] German P. 502,844 (1925) to J. Brode and C. Wurster (to I. G.), *C. A.*, 24, 5441; U. S. P. 1,962,194 (1934) to J. Brode and C. Wurster (to I. G.), *C. A.*, 29, 561; French P. 645,835 (1927) to I. G., *C. A.*, 23, 1998; Swiss P. 143,564 (1931) to I. G., *C. Z.*, 1931 I, 2915.

and chlorine may be used.[83] Another modification involves passing the carbon monoxide-chlorine mixture over a catalyst which accelerates formation of phosgene, and then passing the resulting hot gas mixture over the alumina.[84] The supply of carbon monoxide for the process may be obtained by having excess carbon in the furnace, and keeping the temperature high.[85]

A two-stage process is described by the Niagara Smelting Corporation.[86] When the aluminous mineral contains both alumina and aluminum silicate, preliminary treatment with carbon monoxide and chlorine volatilizes the alumina and iron present; and aluminum silicate left as residue is then treated with chlorine in presence of carbon. Here carbon monoxide is generated and is recovered for use in the first step of the process.

It has been found [87] that the best temperature for the chlorination of alumina silicate with carbon monoxide and chlorine is 1000-1150°. A chlorine-resistant, vitreous, siliceous material was used to line the reaction chamber.[88]

Aluminum chloride may be readily produced by chlorination of Moscow coal ash with simultaneous introduction of carbon.[89]

The use of producer gas for conversion of alumina into aluminum chloride is specified by King and Roberts.[90] Producer gas at a temperature of above 1000° is mixed with chlorine, and the mixture is brought into contact with alumina.

In another process, a mixture of carbon monoxide, oxygen, and chlorine in the ratio 2:1:1 is used. Bauxite is heated in a rotating furnace with the flame produced by the combustion of the gaseous mixture to give aluminum chloride and a residue of silica.

The production of aluminum chloride by reaction of aluminum materials with phosgene has been investigated by Budnikov.[91] When a mixture of bauxite and coal was treated with phosgene at 1000°, a 98.3 per cent of theoretical yield of aluminum chloride was secured. At 1000° for one hour, the best yield from clay, alone, was 35.8 per cent of theoretical When coal was also present, however, the yield rose to 98 per cent at 1000°, and then fell to 56.3 per cent at 800°. Adadurov [92] explains this decrease in conversion by pointing out that at 800°, the dissociation of phosgene is just beginning and that, consequently, there is much less

[83] U. S. P. 1,809,158 (1931) to J. Brode and C. Wurster (to I. G.), *C. A.*, 25, 4365; British P. 281,491 (1927) to I. G., *C. A.*, 22, 3497; German P. 524,712 (1926) to J. Brode and C. Wurster (to I. G.), *C. A.*, 25, 4365.

[84] German P. 525,860 (1927) to J. Brode and C. Wurster (to I. G.), *C. A.*, 25, 4668.

[85] German P. 527,035 (1928) to J. Brode and C. Wurster (to I. G.), *C. A.*, 25, 5254.

[86] U. S. P. 1,875,105 (1932) to G. D. Muggleton, P. S. Brallier, H. C. van Glader, and R. F. Weber (to Niagara Smelting Corp.), *C. A.*, 26, 6079.

[87] P. P. Budnikov, *J. Applied Chem. (U.S.S.R.)*, 6, 1043-1048 (1933); *C. A.*, 28, 4182.

[88] P. P. Budnikov, *loc. cit.* P. P. Budnikoff, *Sprechsaal Keramik, Glas, Emaul.*, 67, 135-136; *C. Z.* 1934 II, 423.

[89] P. P. Budnikov and M. I. Nekritsch, *J. Chem. Ind. Russ.*, 9, No. 12, 14-15 (1932); *C. Z.*, 1934 I, 1094.

[90] Can. P. 223,316 (1922) to G. H. King and G. I. Roberts, *C. A.*, 16, 4022; U. S. P. 1,308,080 (1919) to G. H. King and G. I. Roberts, *C. A.*, 13, 2262.

[91] P. P. Budnikov, *Z. angew. Chem.*, 37, 100-101 (1924), *C. A.*, 18, 2058.

[92] I. E. Adadurov, *J. Chem. Ind. (Moscow)*, 5, 1288-1292 (1929); *C. A.*, 23, 3303.

nascent chlorine present than at 1000°. The role of carbon in the reaction was explained by assuming the reaction

$$Al_2O_3 + 3COCl_2 \qquad 2AlCl_3 + 3CO_2$$

to be reversible, some of the aluminum chloride formed being converted to alumina by the carbon dioxide present. In the presence of coal, however, the carbon dioxide is reduced to the monoxide by the carbon; conversion of aluminum chloride into alumina is thus prevented. Adadurov found that the reaction proceeded most efficiently when charcoal and clay were cemented with crude oil into porous briquets which absorb chlorine. The presence of 5-10 per cent of potassium chloride was reported to catalyze the reaction; an improved yield was obtained, and a lowering of operating temperatures was made possible.

According to Treadwell and Terebesi,[93] the rate of chlorination of alumina with carbon monoxide depends upon the form of alumina which is used. Above 800°, the reaction with γ-alumina is proportional to time; at lower temperatures, however, the reaction is autocatalytic, possibly because of the formation of a layer of active carbon on the alumina. At 650°, γ-alumina is transformed into the less active α-alumina. At this point, therefore, the rate of chlorination is at a minimum. It is maximum at 550°. Chlorination with phosgene was shown to be more rapid than with mixtures of carbon monoxide and chlorine, the maximum lying within the range of existence of phosgene. The rate of chlorination falls at higher temperatures and approaches that of carbon monoxide and carbon at 700°

Much work has been done on the utilization of waste products obtained by the manufacture of aluminum chloride by treatment of clay with chlorine and carbon monoxide.[95]

Reaction of Alumina or Aluminiferous Ores and Miscellaneous Chlorides

When carbon tetrachloride is passed over alumina, even below red heat, it attacks it to yield aluminum chloride, the reaction proceeding with formation also of phosgene, carbon dioxide, hexachloroethane,[96] carbon monoxide, and chlorine.[97] The reaction has been effected by placing an open vessel holding the powdered oxide in a glass tube, driving out the air with a carbon tetrachloride vapor, and then gradually heating the tube while carbon tetrachloride is passed through the tube. At 390°, carbon tetrachloride converts alumina completely into aluminum chloride.[98] Naturally occurring oxides, if finely divided, are transformed into chlorides in the same manner as is alumina. The extent of action on

[93] W. D. Treadwell and L. Terebesi, *Helv. Chim. Acta*, **15**, 1353-1362 (1932); *C. A.*, **27**, 1808.
[95] P. P. Budnikov and M. Ya. Solomin, *Keram i. Steklo*, **9**, No. 9, 9 (1933); *C. A.*, **28**, 3201. P. P. Budnikov and M. Ya. Solomonov, *Keram Rundschau*, **42**, 46, 247 (1934); *C. A.*, **28**, 4555, 5196. I. E. Adadurov, P. P. Budnikov, and A. I. Ryabchenkov, *J. Applied Chem. (U.S.S.R.)*, **7**, 1147-1152 (1934). P. P. Budnikov, *Zement.*, **23**, 740-750 (1934), *Brit. Chem Abs.*-**B**, 547 (1935). P. P. Budnikov and A. B. Kvitnitskii, *Ukrain. Khim. Zhur.*, **10**, 266-270 (1935), *C. A.*, **30**, 2722. B P. Bruns and E. G. Shatunovskaya, *J. Chem. Ind. (Moscow)*, **7**, 34-36 (1932); *C. A.*, **26**, 3708.
[96] E. Demarcay, *Compt. rend.*, **104**, 111-113 (1887); *J. Chem. Soc. Abs.*, **52**, 329 (1887).
[97] L. Meyer, *Ber.*, **20**, 681-683 (1887), *J. Chem. Soc Abs.*, **52**, 552 (1887).
[98] P. Camboulives, *Compt. rend.*, **150**, 175-177 (1910), *C. A.*, **4**, 1433.

anhydrous silicates is in inverse ratio to the silica content; from bauxite containing 3 per cent silica, a definite amount was removed as silicon chloride.[99]

Phosphoryl chloride attacks alumina at 100° and at ordinary temperature, but the rate of reaction is slow.[100] When feldspar is heated with phosphoryl chloride and phosgene at 600°, aluminum chloride is formed, together with potassium chloride, silica, and phosphorus pentoxide. At white heat, phosphorus pentachloride converts alumina partially into aluminum chloride, and partially into aluminum phosphate.[101]

Finely divided alumina, mixed with ammonium chloride and heated to glowing is partially volatilized as the chloride.[102] Boron trichloride attacks alumina at high temperatures to yield aluminum chloride and aluminum borate. Porcelain is similarly attacked, with formation of aluminum chloride, silicon tetrachloride, aluminum borate, and an aluminum-alkali double chloride. Aluminum chloride is also produced by reaction of silicon tetrachloride at the same temperatures with amorphous or crystalline alumina, but not with aluminum silicate or porcelain.[103] At red heat silicon tetrachloride and alumina yield aluminum chloride and crystalline silica, together with a small amount of silicate.[104]

Conversion of Various Aluminum Compounds to Aluminum Chloride

Although the great majority of laboratory and technical preparations of aluminum chloride involve halogenation of either metallic aluminum or aluminiferous ores, various aluminum salts, carbides, nitrides, and silicides have been used. As in syntheses effected with aluminum or its ores, the halogenating component may be chlorine, hydrogen chloride, or metal chlorides. These methods are summarized:

Table 43

Aluminum Compound	Chlorinating Component	Reference
Aluminum fluoride	ammonium chloride	Norw. P. 45,918 (1928) to T. Greiff, *C. A.*, 25, 1341
Aluminum carbide	hydrogen chloride	German P. 325,474 (1920) to Standard Oil Co *C. Z.*, 1920 IV, 525.
Aluminum carbide	hydrogen chloride	Brit. P. 109,790 (1917) to Standard Oil Co., *C. A.*, 12, 206.
Aluminum carbide	hydrogen chloride	U. S. P. 1,218,588 (1917) to M. Barnett and L. Burgess, *C. A.*, 11, 1528.
Aluminum carbide	hydrogen chloride	Can. P. 179,145 (1917) to M. Barnett and L. Burgess, *C. A.*, 11, 3394.
Aluminum carbide	chlorine gas	Can. P. 222,320 (1922) to D. F. Smith and H. Essex, *C. A.*, 16, 4022.
Aluminum silicide	hydrogen chloride	U. S. P. 1,566,269 (1925) to L. Burgess, *C. A.*, 20, 482.
Aluminum carbonate	chlorine gas	Japanese P. 31,761 (1917) to Standard Oil Co., *C. A.* 12, 1238.

[99] P. Camboulives, *Compt. rend.*, 150, 221-223 (1910); *C. A.*, 4, 1433. Cf. H. Quantin, *Compt. rend.*, 106, 1075 (1888).
[100] H. Bassett and H. S. Taylor, *J. Chem. Soc.*, 99, 1402-1414 (1911).
[101] G. A. Daubrée, *Ann. Mines (4)*, 19, 692 (1851).
[102] H. Rose, *Pogg. Ann.*, 74, 569 (1848).
[103] L. Troost and P. Hautefeuille, *Ann. chim. phys. (5)*, 7, 476 (1846); *Compt. rend.*, 75, 1819 (1872).
[104] G. A. Daubrée, *Compt. rend.*, 39, 135 (1854).

Table 43—*(Continued)*

Aluminum Compound	Chlorinating Component	Reference
Aluminum nitride	chlorine gas	Brit. P. 160,759 (1921) to Armour Fertilizer Works, *C. A.*, 15, 2530.
Aluminum nitride	chlorine gas	U. S. P. 1,372,332 (1921) to E. C. Baum and D. C. Jones, *C. A.*, 15, 1972.
Aluminum nitride	hydrogen chloride	U. S. P. 1,688,504 (1928) to C. G. Miner, *C. A.*, 23, 244.
Aluminum nitride	hydrogen chloride	U. S. P. 1,754,797 (1930) to C. G. Miner, *Brit. Chem. Abs.*-B, 111 (1931).
Aluminum phosphate	chlorine gas	Can. P. 344,962 (1934) to C. G. Fink and R. E. Vivian, *C. A.*, 29, 2317.
Aluminum phosphate	chlorine gas	German P. 570,229 (1935) to F. Doerinckel and M. Zimmermann (to I. G.), *C. A.*, 29, 5607.
Aluminum phosphate	chlorine gas	Japanese P. 100,832 (1933) to S. Fujino and Y. Kato, *C. A.*, 28, 4848.
Aluminum phosphate	chlorine gas	Brit. P. 347,137 (1930) to I. G., *Brit. Chem. Abs.*-B, 631 (1931).
Aluminum sulfide	chlorine gas	Norw. P. 39,911 (1924) to Alf Sinding-Larsen, *C. A.*, 19, 1242.
Aluminum sulfide	potassium chloride	U. S. P. 1,716,102 (1929) to H. Blumenberg, Jr., *C. A.*, 23, 3780.
Aluminum sulfate	potassium chloride	U. S. P. 1,649,383 (1927) to H. Blumenberg, Jr., *C. A.*, 22, 483.
Aluminum sulfate	ammonium chloride	U. S. P. 1,764,501 (1930) to H. Blumenberg, Jr., *C. A.*, 24, 4125.
Aluminum sulfate	hydrogen chloride	U. S. P. 1,661,100 (1928) to G. S. Tilley, *C. A.*, 22, 1444.
Aluminum sulfate	chlorine gas	U. S. P. 1,640,732 (1927) to H. I. Lea and C. W. Humphrey, *C. A.*, 22, 306.
Aluminum sulfate	sodium chloride	U. S. P. 1,646,733 (1927) to H. I. Lea and C. W. Humphrey, *C. A.*, 22, 306.
Aluminum sulfate	chlorine gas	Russian P. 37,084 (1934) to M. E. Mandenow and A. M. Monosszon, *C. Z.*, 1936, II, 2770.
Aluminum sulfate	chlorine gas	U. S. P. 1,546,280 (1925) to H. I. Lea and C. W. Humphrey, *C. A.*, 19, 2866.
Aluminum sulfate	sodium chloride and chlorine gas	U. S. P. 1,546,290 (1925) to C. W. Humphrey, *C. A.*, 19, 2866.
Aluminum sulfate	sulfur oxides and chlorine gas	U. S. P. 1,558,897 (1925) to H. I. Lea and C. W. Humphrey, *C. A.*, 20, 97.
Aluminum sulfate	carbonyl chloride	P. P. Budnikov, *Z. angew. Chem.*, 37, 100-101 (1924); *C. A.*, 18, 2058.
Aluminum sulfate	sulfur monochloride	P. P. Budnikov, *Z. angew. Chem.*, 37, 100-101 (1924); *C. A.*, 18, 2058.
Aluminum sulfate	sodium chloride and calcium chloride	U. S. P. 1,818,839 (1931) to G. F. Brindley (to Metal Chlorides Corp.), *C. A.*, 25, 5521.
Aluminum sulfate	calcium chloride	Russian P. 16,134 to A. A. Chakin, W. L. Lukaschew, G. W. Blagoweschtschenski, and A. W. Seikowski, *C. Z.*, 1931 II, 755.
Aluminum sulfate	calcium chloride	U. S. P. 1,764,502 (1930) to H. Blumenberg, Jr.
Aluminum sulfate	chloroform	A. Conduche, *Compt. rend.*, 158, 1180-1182 (1914); *C. A.*, 8, 2359.

Recovery of Aluminum Chloride from Hydrocarbon Sludges

Various means have been devised for recovery of aluminum chloride from sludges formed in the treatment of petroleum oils with aluminum chloride. The coky residues may be roasted with limited access of air to form aluminum oxide which is electrolyzed to yield aluminum.[105] The

[105] Can. P. 222,308 (1922) to A. M. McAfee, *C. A.*, 16, 4058; U. S. P. 1,206,874 (1916) to A. M. McAfee, *C. A.*, 11, 300.

catalyst may also be leached out with water and heated to produce hydrogen chloride and aluminum oxide.[106] Another method involves treatment with steam.[107] Dilute hydrogen chloride has been used for dissolving out the aluminum chlorides.[108] The residue may also be treated with a volatile organic solvent such as alcohol or carbon tetrachloride; removal of the solvent leaves the aluminum chloride revivified.[109]

Other methods deal with the volatilization of aluminum chloride by heating the residues to about 510-960°.[110] The volatilization may be effected in a rotating furnace [111] or in a stationary drum provided with an internal rotary camshaft.[112] Heating of the aluminum chloride residues may also be effected by passing them through a heated zone.[113] Hot vaporous products from oil-refining materials or residues or other gaseous mixtures containing aluminum chloride vapors may be led through a tubular heat-radiating chamber, while the interior walls of the latter are scoured by chains to prevent accumulation of solid chloride on them.[114]

The volatilization has also been effected by impinging the residual mixture, while still in fluid condition, against a revolving disk or other surface heated to a temperature sufficient to volatilize the aluminum chloride.[115]

Treatment of petroleum-coke residues containing aluminum chloride with a stream of hot chlorine or hydrogen chloride leads to volatilization of the catalyst and reformation of aluminum chloride.[116] Addition of chlorine or hydrogen chloride subsequent to a pre-heating of the sludge has been claimed to be advantageous.[117] In this way both residual hydrocarbons and the aluminum chloride may be recovered. Sludge or coke-like residues are centrifuged and burned or treated with gasoline to remove the oil which they carry, then treated with sufficient water to hydrate the aluminum chloride and form a concentrated solution. This is heated until decomposed into alumina and hydrogen chloride; the alumina is mixed with raw coke-like residue, and the mixture is acted on with hydrogen chloride at a low red heat.[118]

[106] Can. P. 222,807 (1922) to A. M. McAfee, *C. A.*, 16, 4058; British P. 250,102 (1925) to Gulf Refining Co., *C. A.*, 21, 1007; U. S. P. 1,578,053 (1926) to A. M. McAfee, *C. A.*, 20, 1715.

[107] U. S. P. 1,865,797 (1932) to W. H. Shiffler (to Standard Oil Co. of Cal.), *C. A.*, 26, 4464; U. S. P. 1,760,962 (1930) to E. B. Phillips and J. G. Stafford (to Sinclair Refining Co.), *C. A.*, 24, 3612.

[108] Russ. P. 34,672 (1934) to I. A. Kazarnovskii, G. F. Komovskii, V. P. Kotov, and M. M. Konstantinov; *C. A.*, 30, 2744.

[109] Can. P. 222,806 (1922) to A. M. McAfee, *C. A.*, 16, 4058; U. S. P. 1,202,081 (1916) to A. M. McAfee, *C. A.*, 11, 208. Also *cf.* U. S. P. 1,426,081 (1922) to C. O. Hoover, *C. A.*, 16, 3358.

[110] U. S. P. 1,405,734 (1922) to A. M. McAfee, *C. A.*, 16, 1313; U. S. P. 1,867,823 (1932) to R. A. Halloran and W. H. Shiffler (to Standard Oil Co. of Cal.), *C. A.*, 26, 5199; U. S. P. 1,401,113 (1921) to L. Burgess, *C. A.*, 16, 1011; U. S. P. 1,568,171 (1926) to A. M. McAfee, *C. A.*, 20, 649.

[111] U. S. P. 1,835,279 (1931) to B. E. Carl and W. S. Austin (to Aluminum Chloride Oil Refining Corp.); *Brit. Chem. Abs.*-B, 886 (1932).

[112] U. S. P. 1,955,272 (1934) to B. E. Carl and W. S. Austin (to Aluminum Chloride Oil Refining Corp.); *Brit. Chem. Abs.*-B, 21 (1935).

[113] Can. P. 247,772 (1925) to A. M. McAfee, *C. A.*, 19, 3150; French P. 564,179 to A. M. McAfee.

[114] U. S. P. 1,641,503 (1927) to G. L. Pritchard and H. Henderson, *C. A.*, 21, 3428.

[115] U. S. P. 1,460,110 (1923) to E. V. Owen; *C. A.*, 17, 2955.

[116] British P. 22,923 (1914) to A. M. McAfee, *C. A.*, 10, 1430; U. S. P. 1,814,397 (1931) to A. M. McAfee (to Gulf Refining Co.), *C. A.*, 25, 5255; Can. P. 222,321 (1922) to A. M. McAfee, *C. A.*, 16, 4056; Can. P. 222,318 (1922) to L. S. Abbott, *C. A.*, 16, 4058; British P. 191,582 (1921) to R. Haddan, *C. A.*, 17, 3097; U. S. P. 1,532,018 (1920) to L. S. Abbott, *C. A.*, 14, 1216.

[117] U. S. P. 1,099,096 (1914) to A. M. McAfee, *C. A.*, 8, 2801; U. S. P. 2,113,028 to W. E. Kuentzel (to Standard Oil Co.)

[118] U. S. P. 1,144,804 (1915) to A. M. McAfee, *C. A.*, 9, 2309.

Volatilization of the aluminum chloride may be effected by heating the sludge on the surface of a hot liquid such as molten lead.[119] Or, the sludge may be injected into a bath of the molten lead, and the liberated aluminum chloride condensed.[120] Instead of molten lead, a bath of molten petroleum wax distillate may be used.[121]

The occluded aluminum chloride in petroleum coke may be liberated by oxidizing the carbon to the gaseous state. During this treatment the aluminum chloride is converted to aluminum oxide and chlorine by the oxygen present and by the high temperature used. Upon further heating in a reducing atmosphere, the oxide and the chlorine are recombined to produce aluminum chloride.[122] Substantially the same procedure involves heating oil sludges with access of air and with ignition of the oil vapors evolved to effect removal of oil, in whole or in part. Continued heating in the absence of air effects distillation and recovery of the aluminum chloride.[123]

Several processes deal specifically with recovery of not only aluminum chloride, but also hydrocarbon material from sludges. When spent residues containing aluminum chloride are boiled with oil, the evolved vapors may be cooled to condense aluminum chloride and a high-boiling oil.[124] A green bloom agent has been extracted from the decomposition products of an aluminum chloride sludge formed by heating aluminum chloride with petroleum oil.[125]

Aluminum chloride is liberated from hydrocarbon sludges by subjecting them to simultaneous cracking and hydrogenation. At the same time, lighter saturated hydrocarbons are obtained.[126]

A method for the production of zinc chloride involves heating a mixture of zinc oxide with petroleum coke containing aluminum chloride. Zinc chloride is formed and vaporized.[127]

A number of patents deal specifically with the condensation of the vapors resulting from the volatilization. The vapors may be transmitted laterally into a body of cold gases in slow upward movement,[128] or a water-cooled rotating cylinder may be positioned above the surface of the material undergoing distillation, thus serving to condense the heavy oil and metal chloride vapors.[129]

Preparation of Anhydrous Aluminum Chloride by Dehydration of Aluminum Chloride Solutions

According to Ralston,[130] because of the excessive water of hydration, the preparation of anhydrous aluminum chloride by dehydrating the

[119] U. S. P. 1,520,080 (1924) to G. L. Pritchard and H. Henderson, *C. A.*, **19**, 707.
[120] U. S. P. 1,665,406 (1928) to P. Danckwardt, *C. A.*, **22**, 1848.
[121] U. S. P. 1,430,100 (1922) to E. V Owen, *C. A.*, **16**, 4057.
[122] U. S. P. 1,464,273 (1923) to G. R. Steuart, *C. A.*, **17**, 3248.
[123] U. S. P. 1,520,831 (1924) to A. M. McAfee, *C. A.*, **19**, 726.
[124] U. S. P. 1,534,150 (1925) to A. M McAfee, *C. A.*, **19**, 1779.
[125] U. S. P. 1,944,851 (1934), Can. P. 338,701 to H. G. Smith (to Gulf Refining Co.), *C. A.*, **28**, 2176.
[126] U. S. P. 1,582,131 (1926) to P. S. Danner, *C. A.*, **20**, 2066.
[127] U. S. P. 1,569,729 to P. Danckwardt.
[128] U. S. P. 1,478,750 (1923) to K. P. McElroy, *C. A.*, **18**, 751.
[129] U. S. P. 1,810,648 (1931) to G. Egloff (to Universal Oil Products Co.); *Brit. Chem. Abs.*-B, 330 (1932).
[130] O. C. Ralston, "Anhydrous Aluminum Chloride," Bureau of Mines, Technical Paper 321, Washington, 1923.

hydrate, $AlCl_3.6H_2O$, has never been very successful. Dennis [131] reports that when the hydrate is heated in a stream of hydrogen chloride, the basic salt, but not anhydrous aluminum chloride, is obtained. Hulin [132] claims that the anhydrous compound is obtained by spreading out the hydrated chloride on the hearth of a furnace made of suitable refractories and heated by a burning mixture of equal parts of hydrogen and dry chlorine. In another method, basic chlorides are heated in a stream of air at 100° to drive off most of the water, and then treated with phosgene or a mixture of carbon monoxide and chlorine.[133]

A number of processes deal with the production of anhydrous aluminum chloride from hydrated bauxite, or from aluminiferous ores which previous to halogenation had been treated with aqueous solutions of acids for removal of impurities. Here conversion of alumina is first effected, subsequent halogenation proceeding in customary manner.[134]

Purification of Aluminum Chloride

In the preparation of aluminum chloride from aluminiferous ores, ferric chloride, silicon tetrachloride and titanium tetrachloride may be formed during halogenation. The last two are readily separated because their boiling points are lower than that of aluminum chloride. In spite of the fact that many of the processes which have been described for the preparation of aluminum chloride are directed especially at preventing contamination by ferric chloride, technical aluminum chloride does contain more or less of this impurity. According to Ralston,[135] the separation of ferric chloride from aluminum chloride by repeated sublimation is practically impossible. However, several methods for subliming aluminum chloride for use in Friedel-Crafts reactions have been described.[136]

A number of patents deal with purification of aluminum chloride on an industrial scale. Most of these are based on conversion of ferric chloride to metallic iron by heating with a metal which has more affinity for chlorine than does iron. An early patent [137] describes melting aluminum chloride under pressure, or mixing it with sodium chloride and melting under atmospheric pressure, and suspending aluminum dust in the fused material to reduce the ferric chloride present to metallic iron, which settles out. The purified material is decanted, and aluminum chloride present in the remainder is volatilized. More recently Humphrey and

[131] L. M. Dennis, *Z. anorg. Chem.*, 9, 340 (1895).
[132] U. S. P. 1,304,567 (1919) to P. L. Hulin.
[133] British P. 130,626 (1918); U. S. P. 1,331,257 (1918) to W. Heap and E. Newbery.
[134] British P. 116,312 (1917) to R. Welford, *C. A.*, 13, 63; *Brit. P.* 225,199 (1923) to C. Assoc. *C. A.*, 19, 1932; U. S. P. 1,490,021 (1924) to A. Pedemonte, *C. A.*, 18, 2060; U. S. P. 1,616,549 (1927) to G. L. Prichard and H. Henderson, *C. A.*, 21, 993; Brit P. 295,227 (1927) to T. R. Haglund *C. A.*, 23, 2354; U. S. P. 1,698,334 (1929) to R. de M. Taveau and C. B. Tygert (to the Texas Co.) *C. A.*, 23, 1222; Brit. P. 297,513 (1926) to S. Svendsen (to Clay Reduction Co.), *C. A.*, 22, 3024 Can. P. 288,622 (1928) to E. C. Marburg, *C. A.*, 20, 3542; U. S. P. 1,543,934 (1925) to A. M. McAfee *C. A.*, 19, 2780. S. Bretsznajder, *Przemysl. Chem.*, 20, 253-269 (1936), *Brit. Chem. Abs.*-B, 541 (1937) J. Zawadski and S. Bretsznajder, *Przemysl. Chem.*, 20, 229-238 (1936), *Brit Chem. Abs.*-B, 541 (1937)
[135] O. C. Ralston, "Anhydrous Aluminum Chloride," Bureau of Mines, Technical Paper 321, Washington, 1923.
[136] E. Bulman, *Bull. soc. chim.*, 33, 995-996 (1923), *C. A.*, 17, 2296. C. D. Neniteseu and C. N. Ionescu, *Bull. soc. chim. Romania*, 14, 66-68 (1932), *C. A.*, 27, 1529. M. C. Boswell and R. R. McLaughlin, *Can. J. Research*, 1, 400-404 (1929), *C. A.*, 24, 534.
[137] U. S. P. 409,868 (1889) to Castner.

McKittrick [138] described a similar process and specified for this purpose the use of a retort having two chambers, one of which is heated and the other cooled.

Jacobson and Ralston [139] mix crude aluminum chloride with aluminum powder and resublime the aluminum chloride in an aluminum-lined, or Vitreosil retort, preferably with mechanical stirring.

Another method involves fusion of crude aluminum chloride with a reducing agent such as aluminum, and separation of the metallic iron from the melt by electromagnetic means.[139] Separation of iron from melted aluminum chloride or from a melt of aluminum chloride and aluminum or an alkali chloride may also be effected by passing a direct electric current through to electrolyze out iron.[140]

Crude aluminum chloride has also been purified by distilling it from aluminum turnings in an aluminum vessel, the ferric chloride thus being reduced to iron, which remains with the non-volatile impurities.[141]

Henriques and Thomsen [142] purify aluminum chloride by subliming it from a bath composed of sodium chloride and aluminum chloride. A modification of this process comprises the introduction of chips of aluminum or iron, or passage of reducing gases into the fused mixture of sodium chloride and aluminum chloride and subsequent sublimation of the purified aluminum chloride.[143]

Reduction of impurities has also been effected by passing aluminum chloride or gases containing it at 500° or higher over metallic iron waste.[144] Heating with iron filings may also be effected in a closed apparatus, the aluminum chloride being deposited in an upper section of it.[145] Deville [146] reports that when crude aluminum chloride is mixed with iron filings, and the mixture is melted under pressure, the ferric chloride is reduced to ferrous chloride which is much less volatile than ferric chloride. The resublimed aluminum chloride therefore has a lower iron content and is less colored.

Weaver [147] passes vapors of crude aluminum chloride into a bath of molten aluminum, near the bottom of the bath, and leads off the purified aluminum chloride vapors.

Brode [148] claims the production of substantially pure aluminum chloride by introduction of a gas mixture carrying aluminum chloride contaminated with iron chloride into molten lead at about 400°. The process is claimed to reduce ferric chloride content from 6.5 to 0.16 per cent.

[138] U. S. P. 1,645,143-4 (1927) to C. W. Humphrey and D. E. McKittrick, *C. A.*, 21, 4034.
[139] British P. 343,174 (1930) to I. G., *Brit. Chem. Abs.*-B, 393 (1931); French P. 695,124 (1930), German P. 515,083 (1929) to I. G., *C. A.*, 25, 1644.
[140] U. S. P. 622,500 (1899) to Castner; Polish P. 26,528 (1938) to L. Wasilewsky, A. Kaczorowski, and A. Weber (to Chem. Inst. Badawczy), *C Z.*, 1939 I, 1823.
[141] N. N. Gratsianss'kii, *Ukrain. Khem. Zhur.*, 9, 432-436 (1934), *C. A.*, 30, 2711.
[142] French P. 688,586 (1930) to O. M. Henriques and T. A. Thomsen, *C. A.*, 25, 780.
[143] British P. 343,208 (1930) to I. G., *Brit. Chem. Abs.*-B, 393 (1931); German P. 530,892 (1930) to C. W. Wurster and M. Gruber (to I. G.), *C. A.*, 26, 263; French P. 710,166 (1931) to I. G., *C. A.*, 26, 1400; U. S. P. 1,901,486 (1933) to I. G.
[144] French P. 688,585 (1930) to O. M. Henriques and T. A. Thomsen, *C. A.*, 25, 780.
[145] French P. 594,344 (1925) to L. Giraud.
[146] H. Sainte-Claire Deville, *Ann. chim. phys. (3)*, 46, 445 (1856).
[147] U. S. P. 1,300,396 (1918) to V. M. Weaver, *C. A.*, 12, 1817.
[148] U. S. P. 1,897,199 (1931) to J. Brode (to I. G.), *C. A.*, 26, 1400; German P. 509,150 (1928), British P. 317,889 (1928) to I. G., *C. A.*, 24, 1944.

Here ferrous chloride and lead chloride are formed during the reaction. Both of these compounds are much less volatile than either aluminum chloride or ferric chloride.

When zinc is contacted with liquefied aluminum chloride, iron separates out and zinc chloride is formed, which boils at 732°. Since ferric chloride boils at 315°, and aluminum chloride sublimes at 178°, the difference in volatility is sufficient to prevent contamination of aluminum chloride.[149]

Phosgene, which forms a liquid double compound with aluminum chloride, but not with ferric chloride, has been used as a purifying agent. The liquid compound is separated from insoluble impurities, and the aluminum chloride is recovered by heating the liquid compound to about 60° to effect volatilization of phosgene.[150] A modification of this process specifies treatment with an oxidizing agent such as chlorine during or after the phosgene treatment.[151] Preferential absorption of aluminum chloride may also be effected by contacting aluminum chloride vapors with a non-aqueous liquid such as alcohol, carbon disulfide, or carbon tetrachloride. Ferric chloride is less soluble in these liquids than is aluminum chloride.[152]

[149] French P. 334,132 (1903); *cf.* German P. 380,502 (1920), U. S. P. 1,369,729 (1920) to P. Dankwardt.

[150] British P. 325,440 (1929) to Imperial Chemical Industries, Ltd., N. Bennett and H. Dodd, *C. A.*, **24**, 4125.

[151] U. S. P. 1,914,335 (1933) to C. Winter and N. Roh (to I. G.), *C. A.*, **27**, 4355; Brit. P. 347,510 (1930) to I. G., *C. A.*, **26**, 1723; French P. 710,166 (1931) to I. G., *C. A.*, **26**, 1400; German P. 526,880 (1930) to I. G., *C. A.*, **25**, 4081

[152] U. S. P. 1,647,446 (1927) to E. R. Wolcott (to The Texas Co.), *C. A.*, **22**, 315.

Chapter 21

Notes on Application of Anhydrous Aluminum Chloride

Storage and Transportation of Anhydrous Aluminum Chloride

Since anhydrous aluminum chloride is extremely hygroscopic, much caution must be observed in handling it. In storage, reaction between moisture and aluminum chloride may take place slowly, thus causing the surface of the mass of anhydrous aluminum chloride to become glazed with a coating of aluminum chloride hydrate, $AlCl_3.6H_2O$. As some of the water of hydration penetrates the still anhydrous salt, reaction occurs, with formation of aluminum oxide and hydrogen chloride. After a time so much hydrogen chloride may be evolved that the pressure of the gas bursts the container. The presence of hydrogen chloride in iron containers also results in corrosion.

Anhydrous aluminum chloride must, therefore, be packed in air-tight sheet-iron drums. Conditions which thus insure the absence of moisture permit storing or transportation over long periods of time.

In technical operation, aluminum chloride may be most expediently used by employing a totally enclosed screw conveyor from a hopper to the reaction vessel. If no conveyor is used, charges of aluminum chloride should be prepared in air-tight cans of the proper size. In this way no occasion occurs for exposure of the anhydrous product to air.

Particle Size

Since the activity of a catalyst increases as its surface is increased, finely powdered aluminum chloride is more useful in many reactions than is coarsely ground or lump aluminum chloride. The use of the finely powdered catalyst, however, often results in a rapid reaction which may be undesirable in condensations effected with sensitive materials or with very active compounds. For these reactions, lump aluminum chloride is more efficient than the powdered grade. In many cases both grades of aluminum chloride form, with equal ease, a soluble complex with the diluent or with one of the reactants. Here, of course, the particle size of the aluminum chloride has no effect on the course of the reaction. Neither is it of importance in reactions effected in a ball mill, as for example in phthalic anhydride addition reactions in the absence of diluent.

Influence of Moisture

In most reactions catalyzed by aluminum chloride precautions must be made to insure anhydrous conditions of reactants and catalyst. When

using compounds such as acid halides, which are especially sensitive to moisture, it is wise to attach a drying tube between the condenser and the gas trap to prevent diffusion of moisture. For careful laboratory work it is frequently recommended that the reactants be dried with anhydrous calcium chloride or over metallic sodium. In some cases materials may be dried sufficiently by distillation. Commercial preparations of aluminum chloride, partially decomposed by contamination due to entrance of moisture into containers, may be recognized by the formation of a hard crust. The presence of moisture may be further ascertained by heating a small sample of the aluminum chloride in a test-tube held horizontally over a flame. Only a thoroughly pure, moistureless aluminum chloride will sublime totally without residue.

In spite of the fact that most workers advise complete exclusion of moisture in aluminum chloride reactions, the presence of *traces* of moisture has been found to accelerate, rather than hinder reaction. This is evidenced especially in reactions involving addition to the olefinic double bond. Here the use of hydrogen chloride, or of small amounts of water (resulting in formation of hydrogen chloride by reaction of anhydrous aluminum chloride with water) is sometimes useful in initiating reaction The accelerating effect of moisture has likewise been noted in studying the cracking of paraffinic hydrocarbons. Small amounts of moisture may also facilitate reaction by causing greater solubility of aluminum chloride in the diluent, thus providing more efficient contact of catalyst with reactants. Whereas dry pentane, in the form of vapor or liquid, undergoes little, if any, decomposition in the presence of freshly sublimed aluminum chloride, addition of anhydrous hydrogen bromide, hydrogen chloride, water, hydrated aluminum chloride, or alkyl chlorides results in immediate reaction.[1]

Undoubtedly water does weaken the catalyst by decomposing it. Moreover, it is obvious that in condensations involving reactants, like acyl halides, which deteriorate upon exposure to moisture, anhydrous conditions must be observed.

The Effect of Impurities: Mixed Catalysts

The impurity which is most often present in anhydrous aluminum chloride is ferric chloride. Consequently the effect of this metal halide on Friedel-Crafts reactions has been rather extensively investigated.

In the synthesis of keto-acids, equimolecular mixtures of ferric chloride and aluminum chloride have been found to be less active than aluminum chloride alone.[2] From an extensive investigation of the use of mixed $FeCl_3$-$AlCl_3$ catalysts in the Friedel-Crafts reaction, Riddell and Noller[3] concluded that, with a mixture of aluminum chloride and ferric chloride and excess benzene as solvent, two types of reactions are found:

[1] A. L. Glasebrook, N. E. Phillips, and W. G. Lovell, *J. Am. Chem. Soc.*, [illegible], 1944-1948 (1936)
[2] W. Gallay and G. S. Whitby, *Can. J. Research*, 2, 81-84 (1930), *C. A.*, 24, 2123; *cf.* M. C. Boswell and R. R. McLaughlin, *Can. J. Research*, 1, 400-404 (1929), *C. A.*, 24, 834.
[3] W. A. Riddell and C. R. Noller, *J. Am. Chem. Soc.*, 52, 4365-4369 (1930); 54, 290-294 (1932)

(1) Those in which the decrease is proportional to the amount of ferric chloride added (reactions with all carboxylic acid chlorides with benzene and of benzene with an excess of carbon tetrachloride).

(2) Those in which the yield first decreased, then rose to a maximum at about 50 mole per cent of ferric chloride, and then decreased to the yield secured with pure ferric chloride (reactions with all acid anhydrides, *p*-toluenesulfonyl chloride and of carbon tetrachloride with an excess of benzene).

Reactions effected in carbon disulfide as diluent all appeared to be of the first type.

In an investigation of the efficiency of technical aluminum chloride containing about 1.5 per cent ferric chloride, in the preparation of 4'-bromo-2-benzoylbenzoic acid, by reaction in an iron ball mill, it was found that both technical aluminum chloride and a colorless, screened product gave substantially the same yields of the keto-acid.[4]

A mixed catalyst consisting of nine parts of zinc chloride and one part of aluminum chloride has been found to give good results in the preparation of chloromethyl derivatives by reaction of aromatic hydrocarbons with paraformaldehyde and hydrogen chloride.*

Fused mixtures of sodium chloride with aluminum chloride have been found to be highly efficient in dehydrogenating condensations.†

The use of various metals as promoters for the aluminum chloride-catalyzed isomerization of α-bromonaphthalene to the β-derivative has been found to give increased conversion. Since promoters for aluminum chloride reactions are very infrequently used, the results are of interest[5]:

Promoter	% Yield of β-bromonaphthalene
Antimony	22.5
Molybdenum	25.0
Selenium	16.0
Nickel	25.5
Tungsten	23.5
Chromium	14.4
No promoter	9.1

Because many reactions probably take place simultaneously during the conversion, the function of the promoter is obscure. The promoter may retard side reactions, or accelerate the main reaction.

In a study of the effect of sulfur and halogen compounds of sulfur on aluminum chloride-catalyzed chlorination, sulfur was found to have no effect on the reaction, whereas the presence of the halogen compounds was shown to have a slight retarding action.‡

[4] P. H. Groggins, A. J. Stirton, and H. P. Newton, *Ind. Eng. Chem.*, 23, 893-899 (1931)
* See page 644.
† See page 652.
[5] H. E. Fisher and R. H. Clark, *Can. J. Research*, 17, 251-252 (1939).
‡ See page 613.

Recently, Ott [5a] has reported activation of aluminum chloride by the catalytic influence of the elements of the fourth group of the periodic system.

Purification of Anhydrous Aluminum Chloride

Anhydrous aluminum chloride which has been only partially decomposed by moisture may be made fit for use by repeated sublimation. The anhydrous salt is white when pure and is thus readily distinguished from the technical grade which is ordinarily gray or yellowish to green and contains about 1.5 per cent of ferric chloride. This impurity cannot be removed from anhydrous aluminum chloride by sublimation. Methods for separating ferric chloride usually depend upon reducing it to the less volatile ferrous chloride or to iron. Preferential absorption of aluminum chloride in phosgene or a non-aqueous liquid such as alcohol, carbon disulfide, or carbon tetrachloride may be used. These methods, ordinarily used only on an industrial scale, are described elsewhere.*

The commercially available reagent grade of anhydrous aluminum chloride, containing 0.05 to 0.10 per cent of iron, is sufficiently pure for most purposes.

Effect of Reaction Conditions

Influence of Reactant Quantities.—In alkylation of aromatic hydrocarbons, the presence of a relatively large amount of hydrocarbon with respect to quantities of both the alkylating agent and of the catalyst favors mono-alkylation. In ketone synthesis, and in preparation of keto-acids, however, the reactants may be used in molar quantities, disubstitution occurring only rarely.

Aluminum chloride is used in catalytic proportions in alkylation and in polymerization, but in the synthesis of ketones, keto-acids, and aldehydes, at least one mole of catalyst with respect to the reactants must be used. Whereas the use of more than catalytic percentages of aluminum chloride leads to uncontrollable side reactions in alkylation and polymerization, in many of the other reactions, yields are materially increased, up to a certain point, as the proportion of the catalyst is increased. In any case, optimum percentage of catalyst for each reaction should be determined experimentally in order to avoid charring, resinification, and decomposition or further condensation of the reaction products.

Addition of Reaction Components.—Unless aluminum chloride has a destructive effect on either or both reactants, the order of addition is unimportant. In condensations effected with easily decomposed compounds, such as thiophene or polynuclear hydrocarbons, however, tarring occurs if aluminum chloride is added alone to the compound to be substituted. Better results are secured by adding slowly a suspension of aluminum chloride in a diluent to a mixture of the two reactants. The

[5a] Erwin Ott, *Angew. Chem.*, 54, 143-144 (1941); E. Ott and W. Brugger, *Z. Elektrochem. angew. physik. Chem.*, 46, 105 (1940).

* See page 884.

rate and manner of addition of reactants, in every case, must be regulated so that reaction does not become too violent.

Effect of Temperature.—Temperature has a decided influence on the course of aluminum chloride reactions.

Reaction with active reactants usually proceeds rapidly, with evolution of heat. Rise in temperature to the point at which decomposition occurs must be prevented. This may be effected by cooling the reaction vessel in an ice-bath, by slow addition of the catalyst or reactant to the reaction mixture, or by vigorous stirring. With rapidly reacting substances some or all of these precautions are necessary in order to prevent decomposition, resinification, and charring.

On the other hand, syntheses with slowly reacting materials require external heating, the temperature necessitated being governed by the reaction rate. In alkylations, acylations, or most addition reactions, temperatures of over 90° are rarely needed, whereas in dehydrating and dehydrogenating condensations, temperatures up to 200° are often used. Reactions requiring high temperatures are usually effected in the presence of a $NaCl$-$AlCl_3$ flux.

Reaction Time.—Optimum reaction time can be determined only experimentally. In most Friedel-Crafts reactions, condensation is allowed to proceed until evolution of hydrogen chloride has ceased. In some instances, other devices may be needed for judging completion of the reaction. This may be effected by a rapid analysis of the reaction mixture in order to determine, for example, the amount of unreacted alkyl halide, or by measuring the amount of hydrogen chloride evolved and comparing it with experimentally derived facts concerning hydrogen chloride evolution at the desired stage. In ketone synthesis, also, the end of the reaction is not necessarily the point at which hydrogen chloride evolution ceases. Here self-condensation of the ketonic product may occur; and since this is a dehydrating condensation, the water given off acts on the aluminum chloride present to give off hydrogen chloride.

In most reactions catalyzed by aluminum chloride, yield of the desired product is frequently decreased rather than increased by prolonged heating or standing of reaction mixtures. Certainly, only with very difficultly reacting components is it necessary or advisable to extend the reaction time after evolution of hydrogen chloride has ceased.

Agitation.—Stirring effects a uniform contact of catalyst and reactants and thus accelerates the speed of reaction. The rate of stirring should be kept quite constant; an abrupt increase may cause sudden frothing or refluxing at a dangerous rate. In most cases, shorter reaction time, faster rate of addition of reactants, and better control of temperature is effected by vigorous stirring. In reactions in which the catalyst complex is a solid, the stirrer must be heavy enough to provide for efficient agitation of the reaction mass as it thickens. Hydrogen halide must be freed from the heavy mass continuously as it is evolved, and this can be insured only by very thorough agitation of the rapidly swelling reaction mixture.

Removal of Evolved Hydrogen Halide.—Since Friedel-Crafts reactions are reversible, provision should be made for removing hydrogen halide as it is evolved. In general laboratory practice this may be effected by simply providing an exit for the gas and working under a hood or absorbing the gas in water. A trap is placed between the absorbent and the gas outlet to prevent the absorbent from sucking back. When evolution of hydrogen chloride is extremely great, efficient removal may be effected by connecting the absorption apparatus to a vacuum. The use of a vacuum is also advisable with slow reactions; here the rapid removal of hydrogen chloride accelerates reaction speed.

Hydrolysis of the Reaction Complex.—In Friedel-Crafts reactions a double compound of aluminum chloride with the reaction product is usually formed. This must be decomposed in order to remove the aluminum chloride. The stability of the complex as well as that of the product regulates the manner of decomposition.

Complexes resulting from alkylation are best decomposed or hydrolyzed by cooling and adding small amounts of a cold, dilute hydrochloric acid. In large-scale practice, too rapid addition of the hydrolyzing medium without sufficient agitation may lead to accumulation of evolved hydrogen chloride and heat within the catalyst complex, and thus to disastrous explosion. In ketone synthesis, the catalyst complex may become semi-solid or solid at room temperature. Here it is best to effect hydrolysis while it is still warm. In laboratory procedure, hydrolysis of the catalyst complex is usually effected by pouring the cooled or partially cooled reaction mixture into a mixture of ice and hydrochloric acid.

Recently, it was pointed out[6] that poor yields in Friedel-Crafts reactions, traced back to difficulty in hydrolyzing extremely stable catalyst complexes, may be overcome by the use of wetting agents in the ice-hydrochloric acid mixture. The wetting agent is claimed to facilitate penetration of such very compact reaction masses as those resulting from the reaction of diphenyl ether or coumarone with stearoyl chloride.

Isolation of Product.—Upon decomposition of the catalyst complex, separation of the reaction product may be brought about by one of the following procedures:

(1) The aqueous solution of the aluminum chloride is allowed to form the bottom layer in the reaction or hydrolysis vessel, the solution of the reaction product in the diluent is decanted, and the diluent and unreacted material are distilled off. Here distillation is stopped when the product begins to distil; on cooling, the product is obtained either as a solid mass, or as an uncrystallizable liquid.

(2) The diluent and unreacted material may be distilled off directly from the hydrolysis mixture. In many cases, however, decantation previous to distillation results in purer products.

[6] U. S. P. 2,189,383 (1940) to A. W. Ralston and R. J. Wander Wal (to Armour Co.)

Removal of the diluent and of unreacted material by steam distillation or by distillation under reduced pressure often makes fractionation unnecessary. If the reaction product is solid at ordinary temperature it may be further purified by recrystallization; if liquid, by fractionation. Further purification or separation from isomers may be effected through preparation of the usual derivatives. Alkylation products are best secured in very pure condition as the sulfonates, keto- acids as metal salts, and aldehydes or ketones as bisulfites or semicarbazones.

Diluents and Solvents for Reactions Catalyzed by Aluminum Chloride

As in most catalytic reactions, the use of a diluent or a solvent in aluminum chloride condensations is often essential in order to regulate temperature, reaction velocity, and uniform contact of the catalyst with the reactant. In reactions with liquid aromatic hydrocarbons or their derivatives, the compound which is to be substituted is generally used as diluent. If, however, neither reactant is a liquid at the reaction temperature, or if the use of one of the reactants is otherwise inadvisable, an extraneous, inert diluent is employed.

Solubility data on aluminum chloride, given elsewhere in this book,* indicate the limited solubility of this salt. Friedel-Crafts reactions are generally conducted in carbon disulfide or in excess of the aromatic hydrocarbon employed, although the insolubility of aluminum chloride in these diluents does not make for securing the maximum catalytic activity.

The effect of diluents on Friedel-Crafts condensation and the other reactions effected by aluminum chloride has been pointed out in the more detailed discussions of the individual reactions which are found in this book, and only generalities will be brought out here. Reactions which are not readily effected demand the presence of a diluent, such as carbon disulfide, or benzene. Condensations with benzene or benzene derivatives having negative substituents are generally slower than those with phenols, phenol ethers, polyalkylated benzenes, polynuclear hydrocarbons, thiophene, and furan or other compounds of increased aromaticity. Reaction with the highly active compounds generally is effected most smoothly in diluents which decrease the catalytic activity of aluminum chloride by forming a more or less stable complex with it.

Thus, the use of nitrobenzene as diluent in the reaction of benzene with the highly active benzyl chloride minimizes the reaction velocity, thereby avoiding the formation of high molecular weight condensation products.[7] The mitigating action of nitrobenzene is shown also in the fact that acylation of polynuclear hydrocarbons, which are themselves readily attacked by aluminum chloride, proceeds much more readily in nitrobenzene solution than it does in carbon disulfide.† Other compounds which form complexes with aluminum chloride, such as bromo- or chlorobenzene, also retard reaction rate, and have been consequently used as

* See page 24.

[7] H. C. J. Olivier, *Rec. trav. chim.*, 45, 817-818 (1926), *C. A.*, 21, 2883.

† See page 351.

diluents with rapidly reacting components. The use of ethyl chloride as a solvent in polymerization has been claimed to give smoother reaction.[7a]

That on many occasions the use of a retarding influence in Friedel-Crafts reaction is of utmost importance may be illustrated by the fact that nuclear acylation of phenols was not realized until about a quarter of a century after the announcement of Friedel-Crafts reaction of benzene with acyl halide. In 1877, Friedel and Crafts [8] had stated that aluminum chloride could not be used as a condensing agent with phenolic compounds on account of the reaction of the hydroxy- group with aluminum chloride; and in 1903 their statement had been substantiated by a fruitless attempt to secure a keto- acid by reaction of α-naphthol with phthalic anhydride in the presence of aluminum chloride in carbon disulfide solution.[9] The discovery that acylation of phenols could be effected if nitrobenzene is used as solvent has made possible numerous Friedel-Crafts reactions involving the synthesis of hydroxy- compounds. The commercially important synthesis of aroyl keto- acids was not applied to phenols until 1919, at which time it was found [10] that if acetylene tetrachloride is used as solvent, the reaction of phthalic anhydride with phenols proceeds readily to give excellent yields of the corresponding keto- acids. Acetylene tetrachloride is thus another solvent which has made an indelible impression on the application of the Friedel-Crafts reaction to phenols.

In Friedel-Crafts substitutions of highly reactive compounds, a less active substance may be used as diluent. Thus benzene, which itself undergoes Friedel-Crafts reactions, is often used as diluent in condensations involving the more reactive phenol ethers or polynuclear hydrocarbons. Analogously, mono- or dichlorobenzenes, which are less reactive than benzene, have served as diluents for Friedel-Crafts reactions with benzene.

Comparison of Aluminum Chloride with Similarly Reacting Catalysts

The researches of Friedel and Crafts showed that reaction between chlorinated aliphatic compounds and aromatic hydrocarbons took place in the presence of aluminum chloride, aluminum bromide, or aluminum iodide. Zinc chloride or ferric chloride had a similar effect, but they were weaker catalysts for the reaction. The chlorides of magnesium, cobalt, copper, mercury, and antimony were reported to be without effect.[11] Later [12] they found that for condensation of the rapidly reacting benzyl chloride with benzene, the chlorides of zinc, the two chlorides of iron, and that of cobalt behaved similarly to aluminum chloride, but that the action was not so energetic. Zirconium chloride, on the other hand, gave results which were as good as those secured with aluminum chloride.

[7a] U. S. P. 2, 240, 583 (1941) to W. J. Sparks and D. C. Field, assignors to Standard Oil Development Co.
[8] C. Friedel and J. M. Crafts, *Compt. rend.*, 84, 1453 (1877).
[9] C. Deichler and C. Weissmann, *Ber.*, 36, 547-560 (1903).
[10] F. Ullmann and W. Schmidt, *Ber.*, 52, 2098-2118 (1919).
[11] C. Friedel and J. M. Crafts, *Compt. rend.*, 85, 74-77 (1877).
[12] C. Friedel and J. M. Crafts, *Bull. soc. chim.* (2), 30, 140 (1878).

Although this book deals with aluminum chloride, the most commonly used Friedel-Crafts type catalyst, a comparison of aluminum chloride with other catalysts is of interest. Thus, Grosse and Ipatieff [13] found that the efficiency of various metal halide catalysts for the alkylation of benzene with ethylene was as follows:

Catalyst	Temp (°C)	Moles of ethylene converted per mole of catalyst
$BeCl_2$	200	50
BF_3	25	35
$AlCl_3$	75	75
$TiCl_4$	170	5
$ZrCl_4$	100	90
$CbCl_5$	75	25
$TaCl_5$	75	60

Calloway [14] indicates that the order of activity of metal chlorides in Friedel-Crafts reactions is as follows:

$AlCl_3$
$FeCl_3$
$ZnCl_2$
$SnCl_4$
$TiCl_4$, $ZrCl_4$

Calloway bases his conclusions on observations as reported for many types of condensations.

Unfortunately data of this nature are not available for all the reactions catalyzed by aluminum chloride. Also it must be borne in mind that, whereas a mild catalyst may be inefficient for some Friedel-Crafts reactions, it may be especially suitable for condensations in which one or both of the reactants are highly active. Acylation of thiophene, for example, is best effected in the presence of catalysts which are less active than is aluminum chloride.

A summary of some reported uses of the more important "Friedel-Crafts" type catalysts follows:

Other Aluminum Halides.—Aluminum bromide is a more active catalyst than aluminum chloride. Whereas the chloride is substantially insoluble in hydrocarbons, aluminum bromide is quite soluble. This difference in solubility accounts for the fact that in physicochemical studies of Friedel-Crafts reactions, aluminum bromide is necessarily used as catalyst. It has been used for almost all the type reactions which are catalyzed by aluminum chloride; in some of the more easily effected condensations, however, aluminum chloride is preferred as a less drastic catalyst.

Although Friedel and Crafts indicated that aluminum iodide may be substituted for aluminum chloride, little is known of the comparative activity of the two halides.

[13] A. V. Grosse and V. N. Ipatieff, *J. Org. Chem.*, 1, 559-566 (1937).
[14] N. O. Calloway, *Chem. Rev.*, 17, 376 (1935).

Aluminum fluoride has been found to be inactive for the acetylation of benzene or anisole,[15] and it does not catalyze the polymerization of cyclopentadiene.[16]

Ferric Chloride.—In 1897, Nencki [17] pointed out that ferric chloride, being a milder catalyst than aluminum chloride, was applicable to syntheses in which aluminum chloride was too drastic. The use of ferric chloride in the synthesis of diphenylmethane, benzophenone, or acetophenone has been found to result in yields which were usually about half of those obtained when aluminum chloride was used,[18] although previously [19] it had been reported that the action of ferric chloride in Friedel-Crafts ketone synthesis is precisely similar to that of aluminum chloride. Ferric chloride has been found to be a much poorer catalyst than aluminum chloride in the preparation of *o*-benzoylbenzoic acid. It does not catalyze the alkylation of benzene with ethylene.[20]

Antimony Chlorides.—Friedel and Crafts reported that the chlorides of antimony did not catalyze Friedel-Crafts reactions. It was later found, however, that antimony pentachloride may be used in acylations.[21] Antimony trichloride may be used in the ketone synthesis and in the reaction of benzene with benzoyl chloride, but is slower and usually requires a higher temperature than does aluminum chloride.[22]

Zinc Halides.—Zinc chloride was used by Friedel and Crafts for the reaction of benzyl chloride with benzene, but Wertyporoch and his coworkers [23] did not find it to catalyze this reaction or that of chloroform with benzene. It has been used in the reaction of allyl chloride with benzene to yield a mixture of chloropropylbenzene and propenylbenzene,[24] as well as for polymerization [25] and isomerization of hydrocarbons.[26]

Zinc fluoride has been investigated by Calloway,[27] who found it to be a good catalyst for the reaction of *tert*-butyl chloride with anisole. This reaction, in which both reactants are very active, requires only a feeble catalyst.

Stannic Chloride.—The mild catalytic activity of stannic chloride has been utilized in the acylation of thiophene, which is more reactive than benzene in Friedel-Crafts reactions.[28] The halide is also useful in acylating or alkylating benzene derivatives having activating substituents, but is not active enough to catalyze satisfactorily Friedel-Crafts reactions with aromatic hydrocarbons that require more drastic conditions.[29] It

[15] N. O. Calloway, *J. Am. Chem. Soc.*, 59, 1474-1479 (1937).
[16] H. Staudinger and H. A. Bruson, *Ann.*, 447, 110-122 (1926); *C. A.*, 20, 2148
[17] M. Nencki, *Ber.*, 30, 1766-1768 (1897).
[18] E. Wertyporoch, I. Kowalski, and A. Roeske, *Ber.*, 66, 1232-1238 (1933); *C A*, 28, 1026
[19] J. Bdzeoken, *Rec. trav. chim.*, 22, 313-317 (1903).
[20] W. Gallay and G. S Whitby, *Can J. Research*, 2, 81-84 (1930); *C. A.*, 24, 2123
[21] W. J. Comstock, *Am. Chem. J.*, 18, 547-552 (1896); *J. Chem. Soc. Abs*, 70 (1), 613 (1896)
[22] B. N. Menshutkin, *J Rus. Phys.-Chem Soc*, 45, 1710-1738 (1913); *C. A*, 8, 910 (1914)
[23] E. Wertyporoch, I. Kowalski, and A. Roeske, *Ber.*, 66, 1232-1238 (1933).
[24] C. D. Nenitzescu and D. A. Isacescu, *Ber.*, 66, 1100-1103 (1933).
[25] R. E. Burk, H. E. Thompson, A. J. Weith, and I. Williams, "Polymerization," p 80 New York, Reinhold Publishing Corp., 1937.
[26] D. Petrov and M. A. Cheltsova, *Compt rend. acad. sci. (U.S.S.R.)*, 15, 79-84 (1937) *C* 31, 6128.
[27] N. O. Calloway, *J. Am. Chem. Soc.*, 59, 1474-1479 (1937).
[28] Ya. L. Goldfarb, *J. Russ. Phys.-Chem. Soc.*, 62, 1073-1082 (1930); *C. A*, 25, 2719.
[29] G. Stadnikoff and A. Baryschewa, *Ber.*, 61, 1998-1999 (1928).

catalyzes Friedel-Crafts reactions with furan.[30] Since tin tetrachloride is very soluble in most organic solvents and can be easily removed from solution it is valuable as a polymerizing agent.[31]

Titanium Chloride.—Titanium chloride is a more feeble catalyst for Friedel-Crafts reactions than is aluminum chloride. It catalyzes the easily activated reaction of thiophene with benzyl chloride; that of benzene with benzyl chloride, however, is less readily effected by this catalyst. It does not catalyze the reaction of benzoyl chloride with benzene.[32] It is only a very feeble catalyst for the reaction of ethylene with benzene.[33] Titanium chloride has been claimed as catalyst for the polymerization of isobutene [34] and of vinylacetylene.[35]

Zirconium Tetrachloride.—The good results obtained by substituting zirconium chloride for aluminum chloride had been noted by Friedel and Crafts. More recently, it has been observed [36] that zirconium tetrachloride may be used in place of aluminum chloride in condensations involving

(a) elimination of hydrogen chloride (preparation of acetophenone, benzophenone, anisaldehyde, and diphenylmethane);
(b) elimination of water (preparation of phenolphthalein);
(c) elimination of alkyl halide (demethylation of anisole);
(d) condensations of phenyl carbamide with benzene and its derivatives.

Zirconium chloride was found to be easily handled and more readily preserved than aluminum chloride.

It has been pointed out [33] that zirconium tetrachloride is more active than aluminum chloride for the alkylation of benzene with ethylene.

Beryllium Chloride.—Because of the position of beryllium in the Periodic Table, beryllium chloride has not generally been considered as a Friedel-Crafts type catalyst. Lately, however, it has been found that this halide catalyzes many of the reactions effected by aluminum chloride, but that higher temperatures and longer time are required for conversion. In some cases better yields and less resinification are secured with beryllium chloride than with aluminum chloride.[37] Grosse and Ipatieff [33] have found beryllium chloride to be less efficient than aluminum chloride in the alkylation of benzene with ethylene.

Boron Trifluoride.—The use of boron trifluoride as a catalyst for the alkylation of phenols and phenol ethers with propylene [38] and for the

[30] H. Gilman and N. O. Calloway, *J. Am. Chem. Soc.*, 55, 4197-4205 (1933).
[31] H. A. Bruson and H. Staudinger, *Ind. Eng. Chem.*, 18, 381-383 (1926). R. E. Burk, H. E. Thompson, A. J. Weith, and I. Williams, "Polymerization," p. 78, New York, Reinhold Publishing Corp., 1937.
[32] G. L. Stadnikov and L. I. Kashtanov, *J. Russ. Phys.-Chem. Soc.*, 60, 1117-1122 (1928); *C. A.*, 23, 2170.
[33] A. V. Grosse and V. N. Ipatieff, *J. Org. Chem.*, 1, 559-566 (1937).
[34] British P. 42,118 (1934) to I. G.; *C. A.*, 29, 3353.
[35] U. S. P. 1,896,182 (1933) to A. S. Carter and F. B. Downing; *C. A.*, 27, 2591.
[36] P. Krishnamurti, *J. Madras Univ.* (1928) (reprint), 5 pages; *Brit. Chem. Abs.*-A, 316 (1929).
[37] H. Bredereck, G. Lehmann, C. Schonfeld, and E. Fritzsche, *Ber.*, 72, 1414-1429 (1939); *Angew. chem.*, 52, 445-446 (1939); *C. A.*, 33, 7745.
[38] F. J. Sowa, H. D. Hinton, and J. A. Nieuwland, *J. Am. Chem. Soc.*, 54, 3694-3698 (1932).

alkylation of salicyclic acid with propylene[39] has been reported to give good results. A very broad patent covers the use of boron halides, instead of aluminum chloride for all Friedel-Crafts reactions, cracking, and addition of hydrogen halides to olefins.[40] Boron fluoride complexes with alcohols and acid anhydrides have been shown to be effective agents for Friedel-Crafts condensations.[41] Boron trifluoride is most used as a polymerizing agent; it has made possible the formation of solid polymeric products from olefins.* Boron trifluoride is a more drastic catalyst for Friedel-Crafts reactions than is aluminum chloride, and for this reason is little used for this purpose.

Hydrogen Fluoride.—In the last few years it has been found that hydrogen fluoride is unusually effective for alkylation of benzene with olefins or alkyl halides,[42] and of cyclopropane and benzene to yield *n*-propylbenzene.[43] It likewise promotes alkylation in the aliphatic series, as is evidenced in the reaction of *tert*-butyl chloride with both trimethylethylene and cyclohexene. Like aluminum chloride, it acts as a dehydrating agent in the alkylation of benzene with *tert*-butyl alcohol.[44] Hydrogen fluoride effects the cyclization of many arylalkyl acids to ketones of the α-hydrindone, α-tetralone, and anthrone types, in yields which are as good as those secured by cyclization of the acid chlorides with aluminum chloride.[45] Its great efficiency is also apparent in the ready acylation of acenaphthene with acetic or benzoic acid. Hydrogen fluoride, however, does not effect the reaction of phthalic anhydride with benzene, or a condensation of benzoic acid with benzene, the addition of naphthalene to succinic anhydride, or a Fries rearrangement of hydroquinone monobenzoate. Aromatic hydrocarbons which, like acenaphthene, contain an alicyclic side ring seem to be unusually amenable to acylation with free acids, acid anhydrides, or acid chlorides in the presence of hydrogen fluoride. Acylation of perinaphthane, and hydrindene takes place with this catalyst at room temperature, but acylation of naphthalene and phenanthrene in the presence of hydrogen fluoride can be accomplished only in a pressure bomb at somewhat higher temperatures.[46] The use of hydrogen fluoride in reactions ordinarily catalyzed by aluminum chloride has been recently summarized by Simons.[47]

[39] W. J. Croxall, F. J. Sowa, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **56**, 2054-2056 (1934).
[40] British P. 307,302 (1928) to F. Hoffmann and C. Wulff; same as German P. 513,414 (1933). *C. A.*, **24**, 127.
[41] H. Meerwein, *Ber.*, **66**, 411-414 (1933).
* See page 797.
[42] J. H. Simons and S. Archer, *J. Am. Chem Soc.*, **60**, 986-987, 2952-2953, 2953-2954 (1938).
[43] J. H. Simons, S. Archer, and E. Adams, *J. Am. Chem. Soc.*, **60**, 2955-2956 (1938).
[44] J. H. Simons, S. Archer, and H. J. Passano, *J. Am. Chem. Soc.*, **60**, 2956-2957 (1938).
[45] L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **61**, 1272-1281 (1939).
[46] L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **62**, 49-53 (1940).
[47] J. H. Simons, *Ind. Eng. Chem.*, **32**, 178-188 (1940); see also J. H. Simons and S. Archer, *J. Am. Chem. Soc.*, **62**, 1623-1634 (1940); J. H. Simons and H. J. Passino, *ibid.*, **62**, 1624 (1940).

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